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# Synthesis and Solution Aggregation Studies of a Suite of Mixed Neutral and Zwitterionic Chromophores for Second-Order Nonlinear Optics

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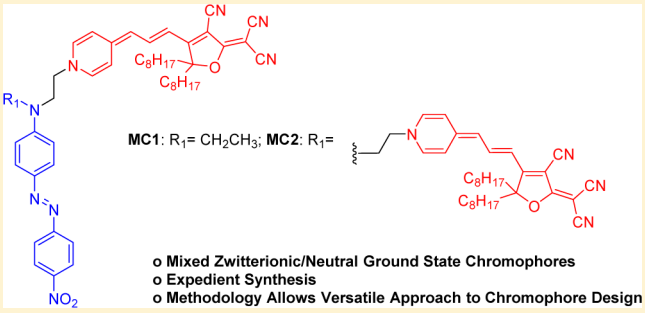
Supporting Information

**ABSTRACT:** We report details of the synthesis of a series of bi- and trichromophores. These compounds contain mixtures of chromophores that have zwitterionic (ZWI) and neutral ground state (NGS) components covalently attached to each other. The neutral ground state moieties are based on dyes with aniline donors—such as Disperse Red 1—whereas the zwitterionic components are derived from chromophores with pro-aromatic donors such as 1,4-dihydropyridinylidene. By combining both ZWI and NGS components, we aim to develop novel compounds for nonlinear optics in which there is an enhancement of the overall hyperpolarizability coupled with a decrease in the net dipole moment. Thus, this approach should eliminate the electrostatic effects that result when only one type of chromophore is used, and so reduce the likelihood of undesirable aggregation occurring. This, in turn, should enable us to realize organic materials with large *macroscopic* optical nonlinearities. An analysis of the UV−vis results suggests that there is a strong dependence on solvent polarity that determines whether the embedded constituents should be treated as discrete elements; in low polarity solvents, there appear to be strong intramolecular interactions occurring, particularly when a 1,4-quinolinylidene-based donor is used in the ZWI component.




## INTRODUCTION

Organic second-order nonlinear optical (NLO) materials have been the subject of considerable research as they are a viable alternative to conventional inorganic crystalline materials in photonic devices.[1−5] This is mainly due to their many advantages when compared to inorganic substrates such as lithium niobate. These include factors such as lower dielectric constants, facile processing, higher electro-optic responses, and reduced production costs. For a chromophore to be suitable for use in NLO devices, it must have a large first hyperpolarizability ($\beta$). However, compounds with high $\beta$ values also tend to have large dipole moments ($\mu$). This results in strong dipolar interactions between the chromophores and encourages antiparallel alignment of the dipoles of neighboring molecules, resulting in a centrosymmetric arrangement and decreased bulk NLO activity.[6−9] This is problematic as, for a bulk material to exhibit an electro-optic response, the constituent chromophores must be aligned in a noncentrosymmetric fashion. Various methods—such as electric-field poling[8] and Langmuir−Blodgett techniques[10]—have been employed to counteract this antiparallel alignment of chromophores, and, therefore, induce noncentrosymmetry. However, such approaches are hindered by the strong electrostatic interactions that occur between the dipoles of the molecules. Thus, while the product of $\mu$ and $\beta$ is often referred to as the figure of merit for a given chromophore, this relationship only holds true in situations when the chromophores have comparatively small dipole moments and are present at low concentrations. Consequently, breaking the antiparallel dimers that form in push−pull chromophores is difficult and the poling process is often an inefficient method for inducing noncentrosymmetry.

As a result, there has been much research into methods to reduce the strong intermolecular interactions that occur between chromophores. They include: site isolation of chromophores via the addition of bulky substituents, which reduce dipole−dipole interactions via steric hindrance;[11−13] designing chromophores with spherically shaped structures, which result in weaker intermolecular dipole−dipole interactions and, therefore, give greater mobility in the poling field;[3,7,14,15] and the development of dendritic chromophores that encapsulate the chromophores inside the dendrimer shell.[5,16,17] Recently, Dalton et al. reported a method for producing chromophores with large $\beta$ values coupled with moderate $\mu$ values by linking neutral ground state (NGS) chromophores with zwitterionic (ZWI) chromophores to give bichromophore **1** (Figure 1).[18] NGS chromophores possess positive hyperpolarizabilities ($+\beta$) along the direction of the

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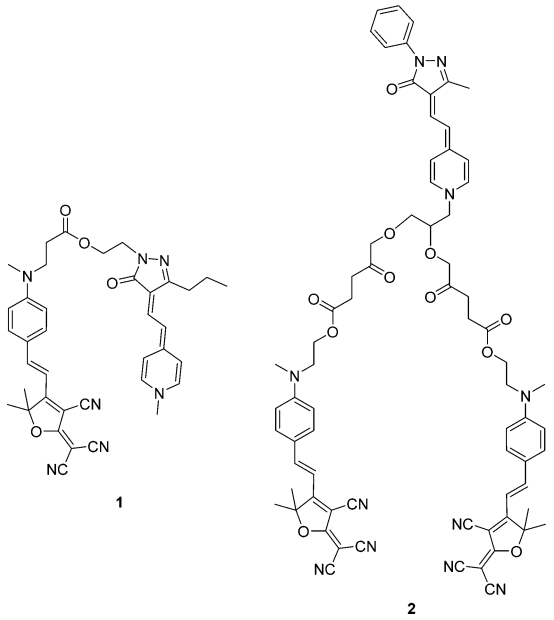

**Figure 1.** Mixed chromophores in the literature. Structures are drawn to show the favored conformations. Note that, in compound **1**, the ZWI component is attached via the donor portion, whereas, in compound **2**, it is attached through the donor nitrogen atom.

dipole moment, whereas ZWI chromophores have negative hyperpolarizabilities ($-\beta$) in the opposite direction to the ground state dipole. In the case of **1**, it was hypothesized that there would be no strong interactions between the components and that they would adopt an antiparallel conformation. This would result in the overall dipole moment being approximately the difference between the $\mu$ values of the two components, while the overall $\beta$ should be the sum of the $\beta$ values of the two chromophores. Indeed, molecular dynamic calculations and NMR and hyper-Raleigh scattering (HRS) studies on compound **1** supported the self-assembly of the bichromophore into an antiparallel conformation in chloroform and indicated that the dipole moment was close to the difference between the two component chromophores while the first hyperpolarizability was close to the sum of them.[18] This, therefore, suggests that this is a valid strategy to simultaneously increase the overall hyperpolarizability and decrease the net dipole moment to give organic NLO materials with large *macroscopic* optical nonlinearities. Thus, this approach should eliminate the electrostatic effects that result when only one type of chromophore is used, and so reduce the likelihood of undesirable aggregation occurring.

Along similar lines, a hetero-trichromophore (**2**) was synthesized by Gao et al. (Figure 1) by linking two NGS chromophores to a ZWI chromophore.[19] Theoretical calculations showed that the total molecular dipole moment was reduced when the chromophores were linked together, with the reported structure adopting a somewhat parallel conformation. From doped polymer films, it was found that a nearly 5-fold enhancement in second harmonic coefficients ($d_{33}$) was realized through this combination of NGS and ZWI chromophores, and this further supports the notion that combining the two types of chromophores can efficiently enhance the macroscopic optical nonlinearity.

Given the promise of the "mixed-chromophore" approach, we report details of the synthesis and of the linear and nonlinear optical properties of a series of "mixed" bi- and trichromophores, containing both NGS and ZWI components (Figure 2). The first set of mixed chromophores, **MC1**−**MC4**, incorporate azobenzene derivatives as the NGS chromophore, while the second group, compounds **MC5**−**MC7**, are derived from 4-vinylaniline-based NGS chromophores. In both groups, the ZWI chromophore components are merocyanines containing tricyanovinyldihydrofuran (TCF)-based electron acceptors. The ZWI chromophore components used in the aforementioned studies by Dalton and Gao and co-workers contained an acceptor derived from pyrazalone (Figure 1). However, previous research conducted in our group has found only very modest figures of merit ($\mu.\beta$) for these types of heteroaromatizable systems.[20,21] In contrast, we have found that merocyanines containing the powerful TCF acceptor have figures of merit of the same order of magnitude as the best NGS examples reported in the literature.[22,23] Therefore, they are a logical inclusion in the current study. It should be noted that donor-$\pi$-acceptor dyes have structures that can be regarded as mixtures of neutral and charge-separated structures and that the terms NGS and ZWI merely describe the dominant contribution. Consequently, the contribution of the two resonance forms to the actual structure very much depends on polarity of the environment. Thus, for example, for ZWI systems in polar media, there will be a very strong contribution from the charge separated form, and this, in turn, will impact on the bond order and observed molecular NLO response.[24]

Additionally, in both the studies by Dalton and Gao and co-workers, the NGS chromophores were derived from 2-(4-(4-aminostyryl)-3-cyano-5,5-dimethylfuran-2(5*H*)-ylidene)-malononitrile, which is in effect 4-vinylaniline attached to a TCF acceptor. We have used this substructure in compounds **MC5** and **MC7**. Azobenzene NGS chromophores derived from Disperse Red 1 (DR1) were used in mixed chromophores **MC1**−**MC3**. DR1 is a well-known standard for organic nonlinear optics, and its ready availability allowed us to easily explore the efficacy of our synthetic approach. The aniline-azobenzene-TCF subunit in **MC4** is also known.[25] It should also be noted that the trichromophore designed by Gao et al. contains two NGS chromophores attached to a ZWI chromophore, whereas, in compounds **MC2** and **MC7**, the reverse applies; i.e., two ZWI chromophores are attached to a single NGS chromophore.

## RESULTS AND DISCUSSION

**Synthesis of Chromophores.** An overview of the synthesis of compounds **MC1**−**MC7** and their precursors is shown in Schemes 1−7. Ful experimental details are included in the Supporting Information. The synthesis of compounds **MC1** and **MC2** is shown in Scheme 1. Activation of the alcohol groups in DR1 and Disperse Red 19 (DR19) was accomplished by converting them to their tosylate derivatives via treatment with tosyl chloride using standard conditions. The isolation of the tosyl derivatives immediately provides a ready route to coupling on the ZWI component as well established merocyanine chemistry often uses the alkyl tosylate (or halide) salts of 2- or 4-picolines as a key synthon. As expected, nucleophilic substitution of the tosyl groups of **3** and **4** by 4-picoline proceeded smoothly to give the 4-picolinium salts **5** and **6**. Building on established chemistry,[22] **5** and **6** were reacted with the *N*-phenylacetamide derivative of TCF, analogue **7**, to give the mixed chromophores **MC1** and **MC2**. It was found that condensation reactions involving **7** were performed most effectively by reacting the acceptor and donor


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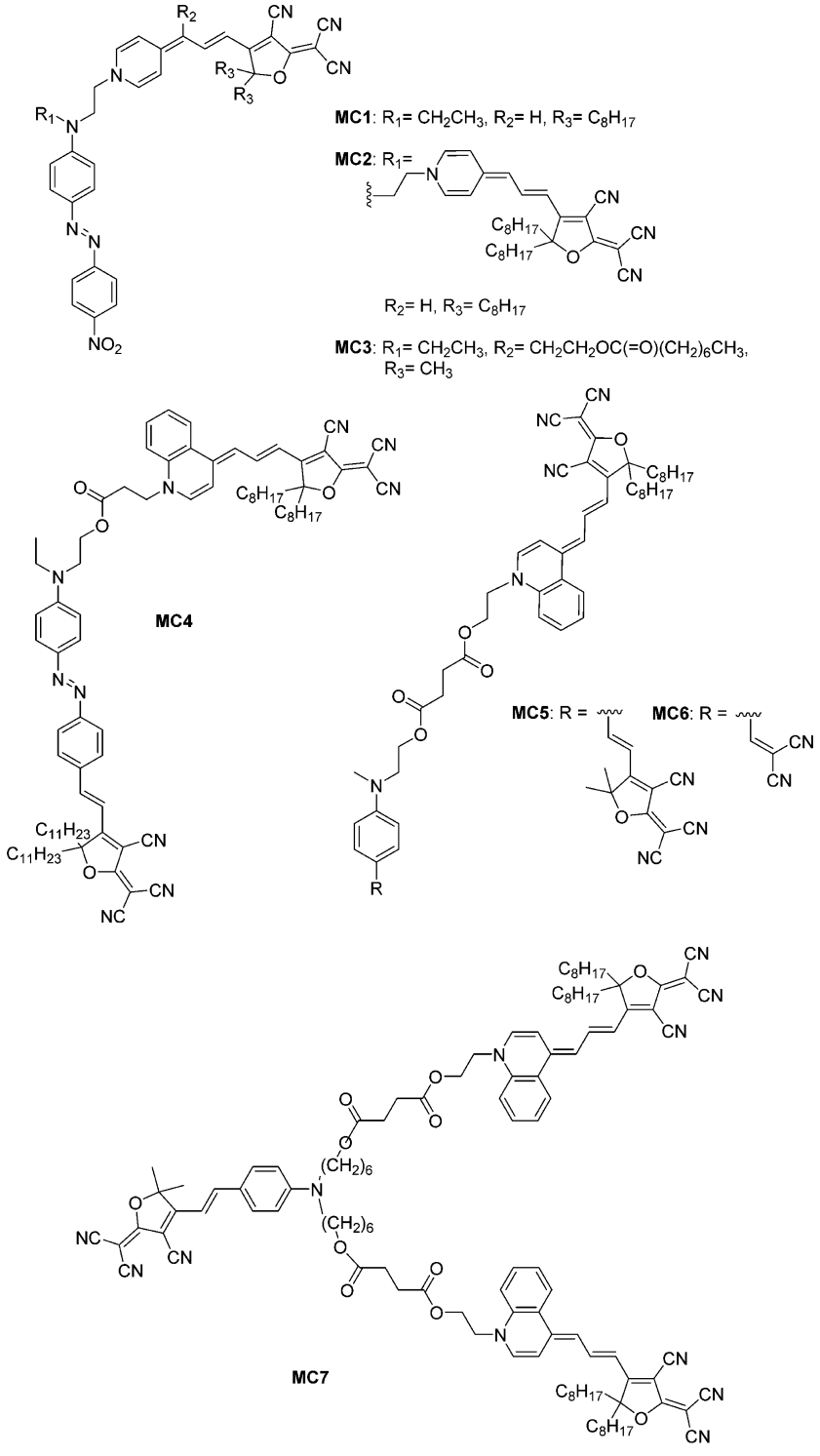


**Figure 2.** Mixed chromophores used in this study. Structures are drawn to represent the favored conformations.

components in anhydrous DCM under $N_2$, with triethylamine as the base.

In the initial part of this study, we used the dimethyl—as opposed to dioctyl—derivative of TCF, which resulted in the synthesis of the dimethyl-TCF analogues of **MC1** and **MC2**. However, the final products were found to have limited solubility and so it was necessary to devise an expedient route to modified TCF acceptors with longer alkyl side chains. The preferred method for synthesis of **7** is shown in Scheme 2.[26] Grignard reaction between the appropriate alkyl magnesium halide and ethyl 2,2-diethoxypropanoate **8**, followed by hydrolysis, gave the hydroxyketones **9** and **10**. Condensation with excess malononitrile gave the modified TCF acceptors, **11** and **12**. The dioctyl acceptor **11** was then reacted with *N*,*N*′-diphenylformamidine in acetic anhydride to give the *N*-phenylacetamide derivative **7**.

The synthesis of **MC3** also used the DR1-tosylate **3** as the starting material. In this case, **3** was coupled with 2-(pyridin-4-yl)ethyl octanoate **14**, prepared from 2-(pyridin-4-yl)ethanol **13**, to give the tosylate salt (Scheme 3). This compound was


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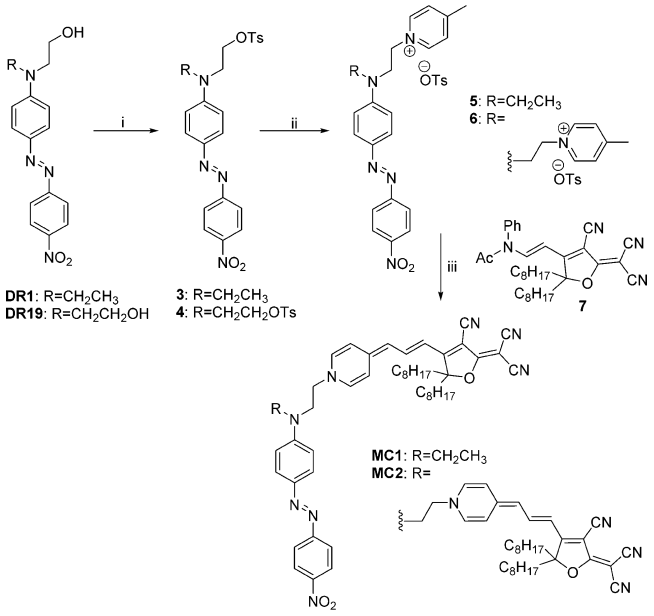
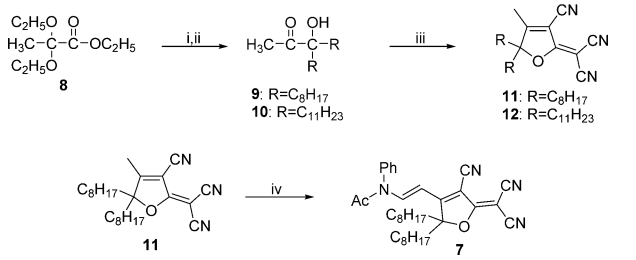
**Scheme 1. Synthesis of MC1 and MC2**[a]




[a]Reagents and conditions: (i) TsCl, $Et_3N$, DCM; (ii) 4-picoline, EtOH; (iii) $Et_3N$, DCM.

**Scheme 2. Synthesis of Modified TCF**[a]

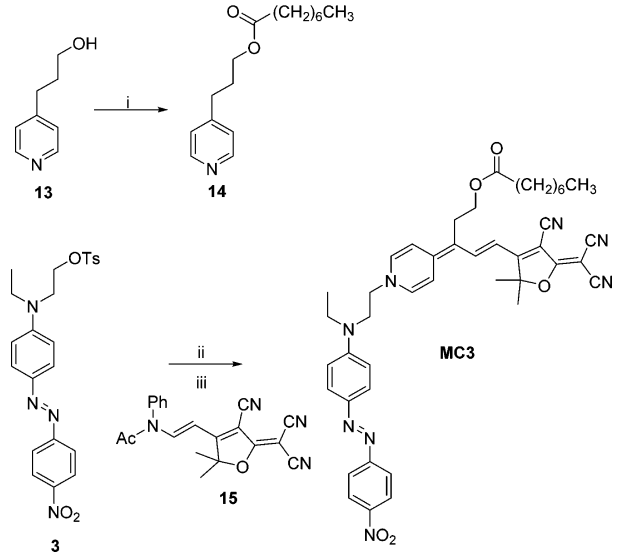



[a]Reagents and conditions: (i) For R = $C_8H_{17}$: 1-bromooctane; for R = $C_{11}H_{23}$: 1-bromoundecane, Mg, diethyl ether, reflux; (ii) EtOH/HCl/$H_2O$, reflux; (iii) malononitrile, $CH_3COOH$, $CH_3COONH_4$, pyridine; (iv) *N*,*N*′-diphenylformamidine, acetic anhydride, reflux.

then condensed with the *N*-phenylacetamide-TCF compound **15**[22] to give **MC3**. The key feature of **MC3** is that it has a long alkyl chain incorporated onto the ZWI chromophore backbone (i.e., the conjugated interconnect) to improve solubility, whereas the related compound **MC1** has long alkyl chains incorporated into it via the dihydrofuran acceptor moiety.

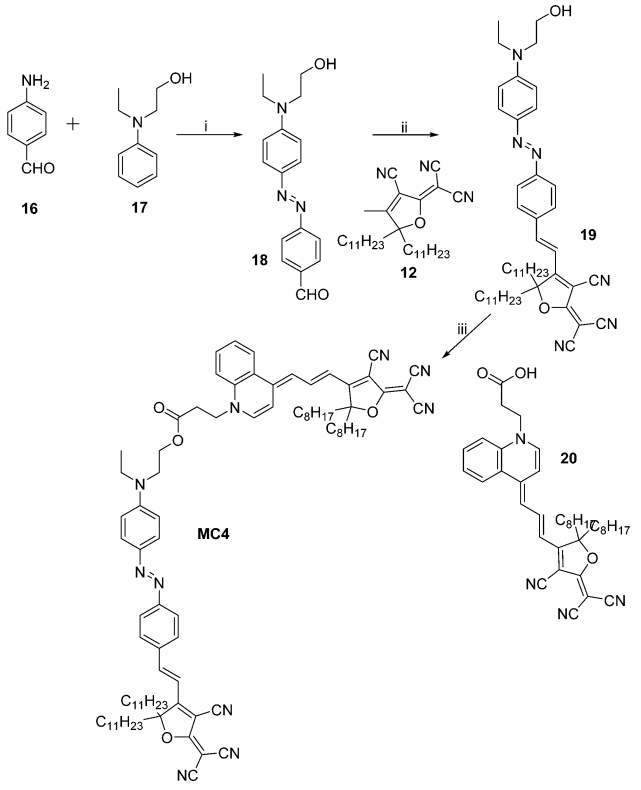
The final compound in the aniline-azobenzene series is chromophore **MC4**, which has a modified TCF with undecyl side chains instead of a simple nitro group as the acceptor component. This compound was synthesized by first coupling the diazonium salt of *p*-aminobenzaldehyde[27] to *N*-ethyl-*N*-hydroxyethylaniline to give **18** (Scheme 4). Condensation of the aldehyde in **18** with the diundecyl TCF acceptor **12** was achieved using triethylamine in methanol to give **19** in 39% yield. The alcohol functional group in **19** was then coupled to the acid-containing chromophore **20**, via a Steglich esterification using EDCI and DMAP to afford **MC4**. Compound **20** was prepared via condensation of 1-(2-carboxyethyl)-4-methylquinolinium bromide with **7** in DCM and using a catalytic quantity of triethylamine (Scheme 5).

**Scheme 3. Synthesis of MC3**[a]




[a]Reagents and conditions: (i) Octanoic acid, EDCI, DMAP, DCM; (ii) **14**, EtOH; (iii) **15**, $Et_3N$, MeOH, reflux.

**Scheme 4. Synthesis of MC4**[a]




[a]Reagents and conditions: (i) $NaNO_2$, $H_2SO_4$, $H_2O$; (ii) $Et_3N$, MeOH; (iii) EDCI, DMAP, DCM.

Compounds **MC5** and **MC6** were synthesized from the NGS chromophores **25a** and **25b**, which were prepared via condensation of 4-(*N*-(2-hydroxyethyl)-*N*-(methyl)amino)-benzaldehyde with TCF or malononitrile, respectively (Scheme 6). It was found that, in order to achieve good yields when coupling the NGS and ZWI components of these mixed chromophores, it was necessary to use a spacer containing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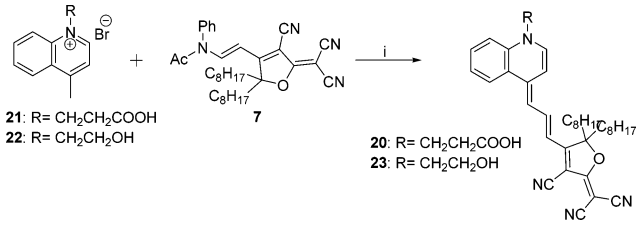
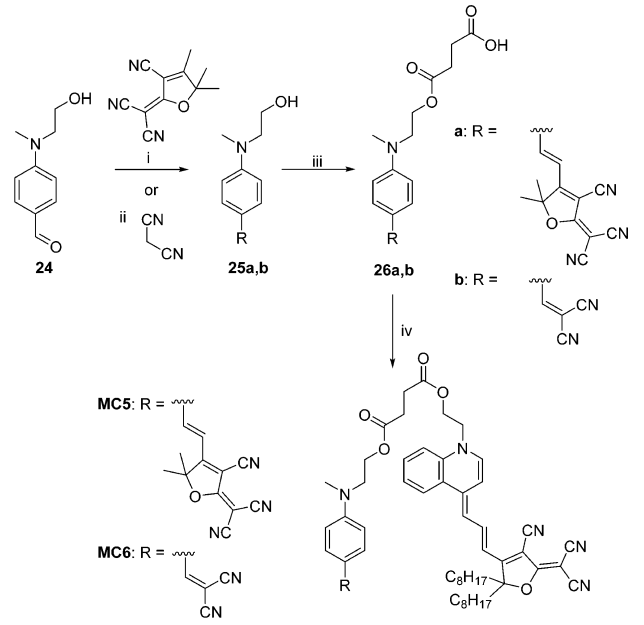
**Scheme 5. Synthesis of Compounds 21 and 24**[a]




[a]Reagents and conditions: (i) $Et_3N$, DCM.

**Scheme 6. Synthesis of MC5 and MC6**[a]

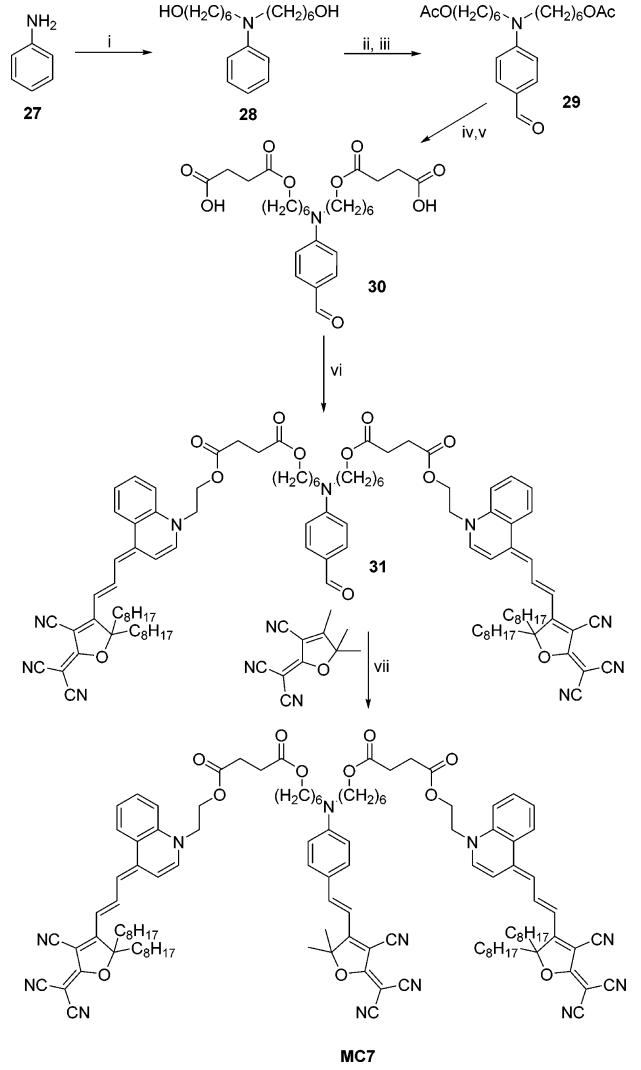



[a]Reagents and conditions: (i) piperidine, EtOH; (ii) $CH_3COOH$, $CH_3COONH_4$, toluene; (iii) succinic anhydride, DMAP, pyridine, DCM; (iv) **23**, EDCI, DMAP, DCM/DMF

approximately 10 carbon/oxygen atoms to extend the distance between the donor groups. Thus, compounds **25a,b** were reacted with succinic anhydride to produce the carboxylic acid functionalized chromophores **26a,b**. Steglich esterification of the acid groups of **26a,b** with the alcohol group of **23**, under EDCI coupling conditions, gave the final compounds **MC5** and **MC6**, respectively. The alcohol containing compound **23** was prepared via condensation of 1-(2-hydroxyethyl)-4-methylquinolinium iodide (**22**) with TCF derivative **7** (Scheme 5).

The synthesis of the final chromophore, **MC7**, commenced with the reaction of aniline with 6-chloro-1-hexanol in *n*-butanol to give diol **28** (Scheme 7). The alcohol groups were then protected by acylation with acetic anhydride before a Vilsmeier formylation was performed to give the aldehyde **29** in 70% yield. The acetyl groups were then removed by base hydrolysis to give the free diol, which was reacted with succinic anhydride to produce the carboxylic acid functionalized chromophore precursor **30**. This was coupled with alcohol **23** to give the ester **31**, which was then converted to **MC7** by reaction with TCF. As there were three sections to be joined together in this compound, each with a strong TCF-based acceptor, the linkage length between the components was longer than was used in compounds **MC5** and **MC6**, which only had two acceptor groups.

**Scheme 7. Synthesis of MC7**[a]




[a]Reagents and conditions: (i) 6-Chlorohexan-1-ol, $K_2CO_3$, aniline, *n*-butanol, reflux; (ii) pyridine, $Ac_2O$, reflux; (iii) $POCl_3$, DMF, 90 °C; (iv) aq. $Na_2CO_3$, MeOH, reflux; (v) succinic anhydride, DMAP, pyridine, DCM; (vi) **23**, EDCI, DMAP, DCM/DMF; (vii) piperidine, $Ac_2O$, reflux.

**NMR Spectral Features.** As might be expected, for many of the final mixed chromophore systems, the NMR spectra are complex due to the size of the molecules. Nonetheless, there are some interesting features that are worthy of further comment. For $^1H$ NMR spectra obtained in $d_6$-DMSO, the olefinic signals arising from the protons on the ZWI $\pi$-interconnect are clearly split into two sets of peaks (generally 1:1), which we interpret as evidence for the presence of two rotamers. This is consistent with previous research in our group that has established that, with, for example, pyridinylidene-TCF type merocyanines, rotational isomerism occurs about the bond that links the TCF ring to the $\pi$-interconnect.[22] Furthermore, in DMSO, the spectra also exhibit very sharp signals for these protons, whereas, for spectra obtained in $CDCl_3$, they are somewhat broader. This phenomenon has been studied by Abbotto et al.[28] and was also observed in the mixed chromophore synthesized by Dalton et al.[18] This is likely due to the fact that, in the more polar solvent (DMSO), the ZWI component exists in a far more charge separated state—i.e.,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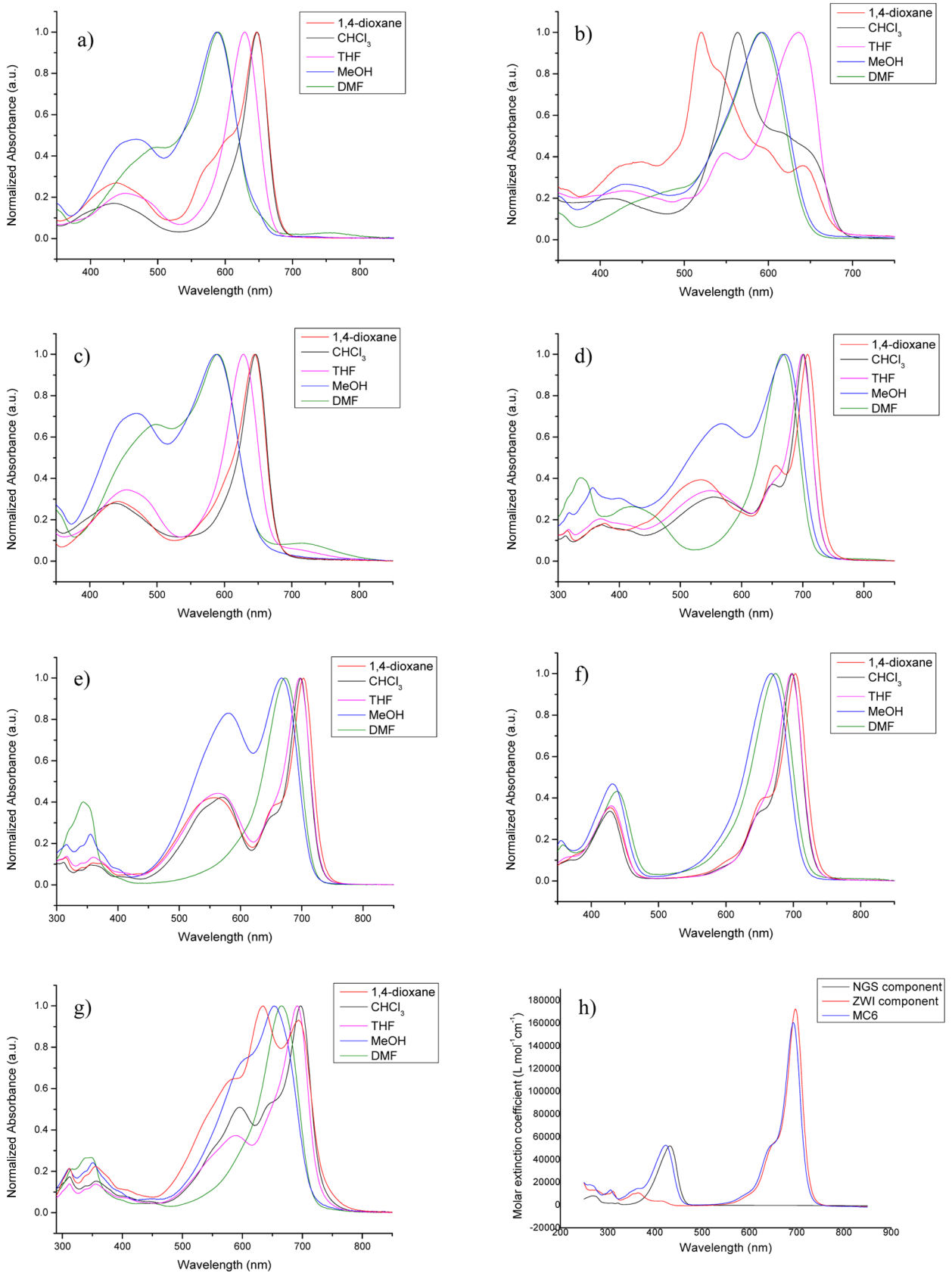


**Figure 3.** UV−vis absorption spectra: (a)−(g) **MC1**−**MC7** in 1,4-dioxane, $CHCl_3$, THF, MeOH and DMF; (h) MC6 and its individual NGS and ZWI components in $CHCl_3$.

polar/zwitterionic state—whereas, in the less polar $CDCl_3$, the ZWI component can be considered as a mixture of the zwitterionic and the quinoidal states.[18] A further point of interest is that rotating frame Overhauser enhancement


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spectroscopy (ROESY) of compounds **MC1** and **MC2** did not exhibit any through-space couplings, which would suggest that the compounds do not adopt a hairpin conformation.

**UV−vis Absorption Studies.** In order to observe phenomena such as solvatochromism and aggregation, the UV−vis absorption spectra of the mixed chromophores were studied across a range of solvents. We chose 1,4-dioxane, chloroform, tetrahydrofuran (THF), methanol, and dimethylformamide (DMF) as they cover a broad range of dielectric constants ($\varepsilon$), namely, $\varepsilon$ = 2.2, 4.8, 7.5, 32.6, and 38.0, respectively. Furthermore, we were also interested to understand whether the component chromophores in all the **MC** compounds behave as discrete, isolated entities, or whether they display spectra consistent with a single, dipolar entity. The results are presented in Figure 3. It should be noted that these spectra have been normalized at their spectral maxima for clarity.

For compounds **MC1** and **MC3**−**MC6**, it was found that, in all solvents, the shape of the absorption spectrum was similar to the superimposed spectra of the NGS and ZWI component chromophores (see Figure 3h for an example), which suggests that there is little orbital overlap and electronic coupling between the two components.[18,29] A similar situation exists for **MC2** and **MC7**, but there are other features in their spectra that warrant more detailed comment later. For compounds **MC1** and **MC3**−**MC6**, across all the solvents studied, the $\lambda_{max}$ corresponds to absorption from the ZWI component. In addition, these absorption maxima showed the expected negative solvatochromic shift, with the wavelength of the absorption maximum generally decreasing with increasing solvent dielectric constant (Table 1). The magnitude of this hypsochromic shift ranged from 30 to 57 nm in going from 1,4-dioxane to DMF. From Figure 3, it is seen that, for **MC4**−**MC6**, the main absorption bands of the spectra obtained in 1,4-dioxane and chloroform are accompanied by a blue-shifted shoulder. The relative intensities of these high energy shoulders and the main absorption bands for **MC4**−**MC6** in 1,4-dioxane and chloroform showed no variation across a range of concentrations, confirming that these shoulders are not due to H-aggregation. Similar high energy shoulders have been reported for the parent ZWI chromophores and have been demonstrated to be associated with changes in the relative probabilities of ground to first excited state vibronic transitions.[30−32] Thus, it is assumed that the blue-shifted shoulders observed here in low polarity solvents are also due to a redistribution of the probabilities of transitions to various vibronic levels and not molecular aggregation.

**Table 1. Absorption Maxima for the Bands Corresponding to the ZWI Components in Compounds MC1−MC7**

| | solvent and absorption maximum (nm) | | | | |
|---|---|---|---|---|---|
| compnd | 1,4-dioxane | $CHCl_3$ | THF | MeOH | DMF |
| **MC1** | 647 | 647 | 629 | 588 | 590 |
| **MC2** | 520 | 563 | 636 | 592 | 591 |
| **MC3** | 645 | 646 | 628 | 588 | 590 |
| **MC4** | 703 | 701 | 695 | 665 | 668 |
| **MC5** | 698 | 698 | 692 | 662 | 668 |
| **MC6** | 698 | 698 | 692 | 662 | 668 |
| **MC7** | 694 | 697 | 692 | 653 | 666 |

It should also be noted that, for some of the ZWI compounds, the observed vibronic structure is indicative of chromophores in which the degree of bond length alternation is quite close to zero, and this would imply that these entities will have a relatively small $\beta$ value. For example, for **MC6**, the spectra shown in Figure 3f suggests that, in low polarity solvents, close to cyanine-like behavior is occurring and that, in order for a stronger NLO response to be observed in the ZWI portion of this compound, it would need to be deployed in more polar solvents. This is also consistent with some of the coupling constants observed in the $^1$H NMR spectra of the "ZWI" components. In these cases—for example, **MC7**—the fact that the coupling constants are essentially the same over both the double and the single bonds of the polyene linker implies very little difference in the bond order.

For compound **MC7**, the absorption maximum observed in 1,4-dioxane is at a shorter wavelength (635 nm) than the maxima obtained in more polar solvents (i.e., 653−697 nm). As noted above, for the ZWI component, a decrease in solvent polarity should lead to an increase in the absorption maximum. Therefore, the absorption maximum in 1,4-dioxane is not due to the unaggregated ZWI component, whose $\lambda_{max}$ occurs at 694 nm in 1,4-dioxane (Figure 3g). In addition, spectra for **MC7** obtained in $CHCl_3$ and THF also contain a blue-shifted shoulder on the ZWI chromophore absorption band. To elucidate this observation, UV−vis absorption spectra of **MC7** were determined in a series of binary liquid mixtures of 1,4-dioxane and MeOH with a range of dielectric constants from 2.94 to 6.96.[33] This showed that the intensity of the blue-shifted band reduces as the dielectric constant increases until it finally merges with the ZWI chromophore band at 690 nm (Figure 4a). Concentration-dependent studies in 1,4-dioxane, $CHCl_3$, and a binary liquid mixture of 1,4-dioxane and MeOH with a dielectric constant of 4.48 showed that the absorption spectral distributions were independent of concentration and confirmed that the blue-shifted band was not due to H-aggregation. Thus, the blue-shifted absorption bands observed in the spectra of **MC7** in low polarity solvents are attributed to redistributed vibronic level transition probabilities, as also seen for the other mixed chromophores **MC4**−**MC6**.

The only chromophores that were found to display molecular aggregation were the DR1-derived compounds **MC1**−**MC3**. Compounds **MC1** and **MC3** exhibited blue-shifted shoulders on the main absorption bands in 1,4-dioxane and chloroform. Concentration studies showed that the absorption spectral distributions were independent of concentration in chloroform. However, in 1,4-dioxane, clear changes in the relative intensities of the shoulder to the main band maxima were observed. It was found that, with increasing concentration, the intensity of the main absorption band was reduced with a concomitant increase in the intensity of the blue-shifted shoulder, confirming H-aggregation.

It is worth noting that, for compound **MC2**, the absorption maxima in both 1,4-dioxane and chloroform occur at shorter wavelengths and with markedly different spectral distributions than is the case for spectra obtained in more polar solvents (Figure 3). Furthermore, concentration studies of **MC2** in 1,4-dioxane and $CHCl_3$ showed that the absorption spectral distributions were independent of concentration, suggesting that aggregation was not responsible for the observed changes in the spectra. In order to understand this further, UV−vis absorption data for compound **MC2** were obtained in a series of binary liquid mixtures of 1,4-dioxane and MeOH with dielectric constants ranging from 2.94 to 17.83 (Figure 4b).[33]


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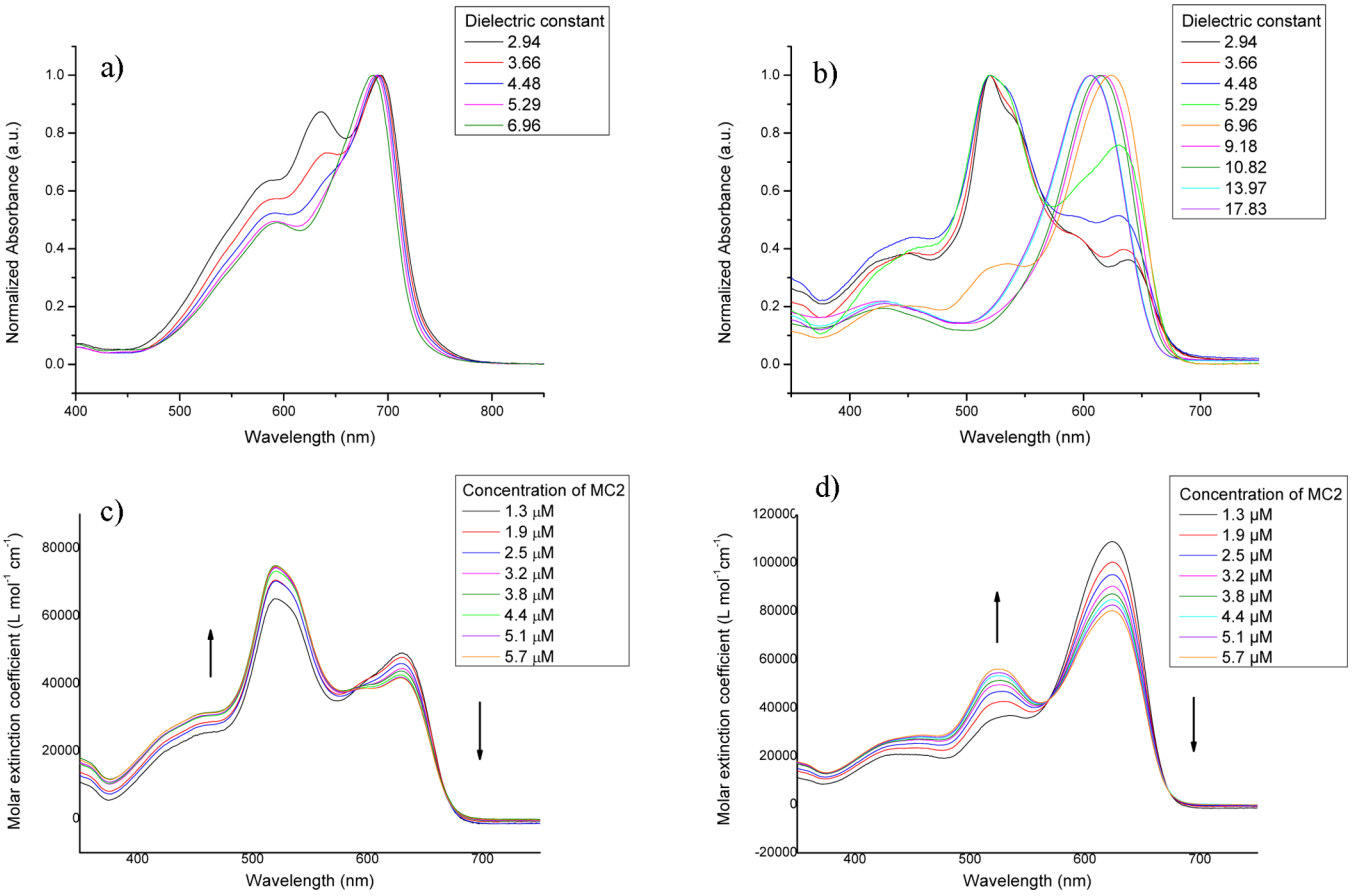


**Figure 4.** UV−vis absorption spectra: (a) Normalized UV−vis absorption spectra of compound **MC7** in a series of binary liquid mixtures of 1,4-dioxane and MeOH with a range of dielectric constants from 2.94 to 6.96. (b) Normalized UV−vis absorption spectra of compound **MC2** in a series of binary liquid mixtures of 1,4-dioxane and MeOH with a range of dielectric constants from 2.94 to 17.83. (c) UV−vis absorption spectra showing the concentration dependence of **MC2** in a binary liquid mixture of 1,4-dioxane and MeOH with a dielectric constant of 5.29 (concentrations ranged from 1.3 to 5.7 $\mu$M). The arrows depict the trend that occurs upon increasing the concentration. (d) UV−vis absorption spectra showing the concentration dependence of **MC2** in a binary liquid mixture of 1,4-dioxane and MeOH with a dielectric constant of 6.96 (concentrations ranged from 1.3 to 5.7 $\mu$M). The arrows depict the trend that occurs upon increasing the concentration.

The spectra in Figure 4b were normalized at the absorption maxima bands for clarity.

From Figure 4b, it is seen that, in the solutions of lowest dielectric constant, 2.94−5.29, the absorption maxima occur at ∼520 nm. However, as the dielectric constant of the solution was increased across this range, so too did the intensity of the band at ∼630 nm. Then, when the absorption spectrum was measured in the mixture with a dielectric constant of 6.96, the absorption maximum shifted to ∼630 nm, and the intensity of the band at ∼520 nm significantly reduced. As the dielectric constant of the binary mixture was further increased, the intensity of the blue-shifted band at ∼520 nm continued to decrease and was no longer apparent at a dielectric constant of 9.18. In addition, in the higher dielectric constant solutions (6.96−17.83), the expected negative solvatochromic shift is observed, with the wavelength of the absorption maximum decreasing with increasing solvent dielectric constant. Thus, in the wavelength region where the absorption maximum switches from 521 to 632 nm upon going from a dielectric constant of 5.29 to 6.96, concentration studies of **MC2** in binary liquid mixtures of 1,4-dioxane and MeOH with dielectric constants of 5.29 and 6.96 were undertaken (Figure 4c,d). Over a wide range of concentrations, well-defined isosbestic points are apparent and which indicate the presence of equilibria between two species.[34] In both solutions, the intensities of the blue-shifted bands (at 521 and 530 nm) increase as the concentration increases, whereas the intensity of the lower energy bands (at 631 and 624 nm) decreases. This is consistent with the formation of H-dimer aggregates, with the hypsochromically shifted band corresponding to the dimer aggregate and the longer wavelength band to the monomer. The dimerization process is very sensitive to the polarity of the solvent, which suggests that dipolar interactions are the main contributor to the dimerization. Furthermore, based on these results, we conclude that, for the spectra we obtained for **MC2** in 1,4-dioxane and $CHCl_3$ and within the range of concentrations used (0.7−3.3 and 1.3−3.3 $\mu$L, respectively), the tendency for molecular aggregation may be so strong as to preclude the experimental observation of the monomers. This is consistent with an absence of a concentration dependence for this chromophore in low polarity environments.

The existence of the dimer aggregate could be attributed to *cis*−*trans* isomerization of the azobenzene group in the structure. This is because only the compounds that were derived from DR1, i.e., **MC1**−**MC3**, exhibited aggregation. There is a large geometrical transformation from the extended, flat *trans* form to the more three-dimensional and compact *cis* isomer of azobenzene compounds.[35] It is proposed that one


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isomer may allow greater interaction between the molecules, such as $\pi-\pi$ stacking, thereby facilitating aggregation. It has been found that increasing the solvent dielectric constant increases the isomerization rate between the two forms, which in terms of the proposed model, is consistent with the sensitivity of dimerization to the polarity of the solvent.[36,37] As noted above, **MC2** was also studied by ROESY NMR. The solvent used for the NMR study was deuterated dichloromethane as **MC2** was insufficiently soluble in more nonpolar solvents such as dioxane, chloroform, and THF. Nonetheless, as the UV−visible absorption spectrum of **MC2** in dichloromethane showed the presence of a dimer, it was deemed a suitable medium. However, no intermolecular cross-couplings could be found, and all ROE signals could be assigned to intramolecular through-space couplings.

In the UV−visible absorption spectra of chromophores **MC1**, **MC3**, and **MC6**, the bands corresponding to the NGS component showed the expected positive solvatochromic shift, with $\lambda_{max}$ for the band generally increasing with increasing solvent dielectric constant (Table 2). A bathochromic shift of

**Table 2. Absorption Maxima for the Bands Corresponding to the NGS Components in Compounds MC1−MC7**

| | solvent and absorption maximum (nm) | | | | |
|---|---|---|---|---|---|
| compnd | 1,4-dioxane | $CHCl_3$ | THF | MeOH | DMF |
| **MC1** | 439 | 435 | 451 | 469 | 499 |
| **MC2** | 447 | 413 | 432 | 430 | N/A[a] |
| **MC3** | 440 | 439 | 452 | 469 | 499 |
| **MC4** | 529 | 556 | 546 | 562 | 420 |
| **MC5** | 552 | 570 | 560 | 576 | N/A[a] |
| **MC6** | 424 | 428 | 425 | 427 | 433 |
| **MC7** | 590 | 595 | 590 | 615 | N/A[a] |

[a]These bands overlap the ZWI band.

59 and 60 nm was observed on going from 1,4-dioxane to DMF for **MC1** and **MC3**, respectively, whereas compound **MC6** showed only a very small shift of 9 nm. The NGS band for compound **MC2** did not obey the expected positive solvatochromic shift, but this may be due to the dimerization observed and discussed above. Compounds **MC4**, **MC5**, and **MC7** also showed the expected bathochromic shift of the NGS band in going from 1,4-dioxane to methanol, with red shifts of 33, 24, and 25 nm, respectively. For compounds **MC5** and **MC7**, the NGS band merges with the ZWI adsorption band in DMF but a high energy peak also appears, at 339 and 348 nm, respectively. These high energy peaks were also observed in the UV−vis spectra of the component NGS chromophores in DMF. These high energy peaks were found to only occur when the NGS chromophore has a terminal TCF group and are attributed to twisted internal charge transfer states.[38,39]

Finally, we have obtained values for the molecular nonlinear response of **MC1**−**MC7** in both DMF and THF, along with data for the constituent ZWI and NGS components. Not surprisingly, given the somewhat complex nature of these molecules, a detailed explanation is required, and this is well beyond the scope of the present study. Nonetheless, the results they do confirm that the polarity of the solvent greatly affects the observed response and that far stronger intramolecular interactions occur in THF than in the more polar DMF. These results will be reported in due course.

## CONCLUSIONS

A series of chromophores containing mixtures of zwitterionic and neutral ground state components covalently attached to each other have been synthesized and characterized. Data obtained from UV−vis absorption spectra show that, in low polarity media, several of the compounds, **MC1**−**MC3**, exhibit behavior consistent with the presence of H-aggregation and that the tendency to form aggregates is so strong that the observation of monomeric species was not possible at the concentrations studied. As a result, we are currently investigating how their molecular NLO properties translate to the bulk level. This will involve incorporation of the compounds in polymer films, followed by electric field poling and measurement of the macroscopic response. As noted above, we have obtained data for the molecular NLO response of the new chromophores, and these results will be reported elsewhere.

## EXPERIMENTAL SECTION

**Materials.** Commercially available reagents were obtained and were used without additional purification. The solvents used were of analytical grade and were also used without further purification. Column chromatography was carried out on Merck silica gel type 9385 (230−400 mesh) with the stated solvent systems. Analytical thin-layer chromatography (TLC) analyses were performed on precoated plates (Merck aluminum sheets, silica gel 60F 254, 0.2 mm). Visualization of compounds was achieved by illumination under ultraviolet light (254 nm). Compounds ethyl 2,2-diethoxypropanoate **8**,[40] **15**,[22] **16**,[27] **21**,[41] **22**,[42] and **24**[43] were prepared according to the literature procedures.

**Measurements and Instrumentation.** Melting points were recorded with an EZ-Melt automated melting point apparatus and are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded on a 500 MHz spectrometer in the deuterated solvent indicated. Chemical shifts are given in ppm (parts per million) and $J$ values in Hz using solvent or TMS as an internal reference. Assignments of protons were confirmed on the basis of DEPT90, DEPT135, and 2D NMR experiments ($^1H-^1H$ COSY, HSQC). Accurate mass measurements were made on a mass spectrometer operating in the positive ion mode. The UV−visible (UV−vis) absorption spectra were recorded by a dual beam spectrophotometer at room temperature over a range of concentrations ($10^{-6}-10^{-7}$ M) with a 10 mm path length quartz cuvette.

**(*E*)-2-(Ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl 4-Methylbenzenesulfonate (3).** To a solution of DR1 (15 g, 48 mmol) and triethylamine (27 mL, 191 mmol) in anhydrous dichloromethane (250 mL) at 0 °C under $N_2$ was added dropwise a solution of tosyl chloride (15 g, 79 mmol) dissolved in a minimum amount of anhydrous dichloromethane. The mixture was warmed to rt and stirred for 16 h. Water (250 mL) was added to quench the reaction and the aqueous layer extracted with dichloromethane twice (250 mL). The combined organic phases were extracted with water three times (500 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give the crude product as a red solid. The crude product was recrystallized from isopropanol to give the pure product **3** as a red solid (21 g, 93%). Spectral properties are in agreement with those in the literature:[44] mp 136−137 °C $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$: 8.32 (2H, d, $J$ = 9.10 Hz, Ar**H**), 7.92 (2H, d, $J$ = 9.10 Hz, Ar**H**), 7.84 (2H, d, $J$ = 9.25 Hz, Ar**H**), 7.73 (2H, d, $J$ = 8.31 Hz, Ar**H**), 7.27 (2H, d, $J$ = 7.95 Hz, Ar**H**), 6.63 (2H, d, $J$ = 9.28 Hz, Ar**H**), 4.22 (2H, t, $J$ = 6.07 Hz, O**CH$_2$**), 3.71 (2H, t, $J$ = 6.07 Hz, N**CH$_2$**), 3.44 (2H, q, $J$ = 7.11 Hz, **CH$_2$**CH$_3$), 2.39 (3H, s, ArC**H$_3$**), 1.19 (3H, t, $J$ = 7.11 Hz, CH$_2$C**H$_3$**). HRMS (ESI): $m/z$ $[M + H]^+$ calcd for $C_{23}H_{25}N_4O_5S$: 469.1546; found: 469.1542 $\Delta$ = 0.8 ppm.

**Disperse Red 19 (DR19).** 4-Nitroaniline was dissolved in 6 M HCl (33 mL) at 0 °C. Sodium nitrite (4.71 g, 68 mmol) was dissolved in iced water (30 mL) and added dropwise to the reaction mixture over 30 min at 0 °C. *N*-Ethyl-*N*-hydroxyethylaniline (13.0 g, 72 mmol)


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was dissolved in 2:1 methanol/water (200 mL) and cooled in an ice bath. The freshly prepared 4-nitroaniline diazonium salt was added dropwise to the reaction mixture over an hour at 0 °C with vigorous stirring. After stirring the mixture for a further 30 min, the precipitate was filtered, washed with water (2 × 200 mL) and recrystallized from acetone to give the product Disperse Red 19 (16.5 g, 77%) as a dark red powder. Spectral properties are in agreement with those in the literature:[45] mp 203−205 °C (lit. 201−203 °C);[45] $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 8.36 (2H, d, $J$ = 9.0 Hz, ArH), 7.93 (2H, d, $J$ = 9.0 Hz, ArH), 7.82 (2H, d, $J$ = 9.2 Hz, ArH), 6.91 (2H, d, $J$ = 9.3 Hz, ArH), 4.84 (2H, t, $J$ = 5.1 Hz, OH), 3.65−3.58 (8H, m, $(CH_2)_2$); HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{16}H_{18}N_4O_4Na$: 353.1226; found: 353.1229 $\Delta$ = 0.9 ppm.

**(*E*)-2,2′-(4-((4-Nitrophenyl)diazenyl)phenylazanediyl)bis-(ethane-2,1-diyl)bis(4-methylbenzenesulfonate) (4).** To a solution of DR19 (10 g, 30 mmol) and triethylamine (17 mL, 121 mmol) in anhydrous dichloromethane (150 mL) at 0 °C under $N_2$ was added dropwise a solution of *p*-toluenesulfonyl chloride (14 g, 76 mmol) dissolved in a minimum amount of anhydrous dichloromethane. The mixture was warmed to rt and stirred for 16 h. Water (150 mL) was added to quench the reaction, and the aqueous layer was extracted with dichloromethane (2 × 150 mL). The combined organic phases were extracted with water (3 × 300 mL), dried over $MgSO_4$, and concentrated in vacuo to give the crude product as a red solid. The crude product was recrystallized from isopropanol to give the pure product **4** as a red solid (13 g, 68%): Spectral properties are in agreement with those in the literature;[46,47] mp 173−175 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.34 (2 H, d, $J$ = 9.1 Hz, ArH), 7.94 (2 H, d, $J$ = 9.1 Hz, ArH), 7.80 (2 H, d, $J$ = 9.2 Hz, ArH), 7.70 (4 H, d, $J$ = 8.3 Hz, ArH), 7.26 (4 H, d, $J$ = 7.9 Hz, ArH), 6.54 (2 H, d, $J$ = 9.2 Hz, ArH), 4.18 (4 H, t, $J$ = 5.8 Hz, $CH_2O$), 3.69 (4 H, t, $J$ = 5.8 Hz, $NCH_2$), 2.39 (6 H, s, $ArCH_3$); HRMS (ESI): $m/z$ $[M + H]^+$ calcd for $C_{30}H_{31}N_4O_8S_2$: 639.1583; found: 639.1594 $\Delta$ = 1.7 ppm.

**(*E*)-1-(2-(Ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)-ethyl)-4-methylpyridinium 4-Methylbenzenesulfonate (5).** Compound **3** (12.0 g, 26 mmol) and 4-picoline (12.4 mL, 128 mmol) were dissolved in EtOH (150 mL) and refluxed for 16 h. The solution was then cooled to room temperature and chilled in a freezer. The product was collected by filtration and washed with cold EtOH (3 × 150 mL) to give **5** as a red solid (11.4 g, 79%): mp 221−223 °C; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 8.93 (2 H, d, $J$ = 5.9 Hz, ArH), 8.38 (2 H, d, $J$ = 8.9 Hz, ArH), 7.97 (2 H, d, $J$ = 6.5 Hz, ArH), 7.95 (2 H, d, $J$ = 9.0 Hz, ArH), 7.81 (2 H, d, $J$ = 9.1 Hz, ArH), 7.49 (2 H, d, $J$ = 7.9 Hz, ArH), 7.11 (2 H, d, $J$ = 7.9 Hz, ArH), 6.89 (2 H, d, $J$ = 9.2 Hz, ArH), 4.78 (2 H, t, $J$ = 6.3 Hz, $CH_2CH_2$), 4.04 (2 H, t, $J$ = 6.3 Hz, $CH_2CH_2$), 3.41 (2 H, q, $J$ = 6.9 Hz, $CH_2CH_3$), 2.58 (3 H, s, $ArCH_3$), 2.28 (3 H, s, $ArCH_3$), 1.08 (3 H, t, $J$ = 7.0 Hz, $CH_2CH_3$); $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$: 159.2, 156.0, 151.1, 147.1, 145.8, 144.4, 143.2, 137.5, 128.2, 128.0, 125.9, 125.5, 125.0, 122.6, 111.8, 57.2, 49.5, 44.4, 21.4, 20.8, 11.7; HRMS (ESI): $m/z$ $[M]^+$ calcd for $C_{22}H_{24}N_5O_2$: 390.1930; found: 390.1923 $\Delta$ = 1.8 ppm.

**(*E*)-1,1′-(2,2′-(4-((4-Nitrophenyl)diazenyl)phenylazanediyl)-bis(ethane-2,1-diyl))bis(4-methylpyridinium) 4-Methyl-benzenesulfonate (6).** Compound **4** (6.0 g, 9.4 mmol) and 4-picoline (9.1 mL, 94 mmol) were dissolved in acetonitrile (120 mL) and refluxed for 72 h. The solution was then cooled to room temperature and chilled in a freezer. The product was collected by filtration and washed with cold EtOH (3 × 100 mL) to give **6** as a red solid (5.6 g, 73%): mp 237−238 °C; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 8.93 (4 H, d, $J$ = 6.4 Hz, ArH), 8.40 (2 H, d, $J$ = 9.0 Hz, ArH), 7.97 (2 H, d, $J$ = 8.9 Hz, ArH), 7.93 (4 H, d, $J$ = 6.4 Hz, ArH), 7.75 (2 H, d, $J$ = 9.1 Hz, ArH), 7.50 (4 H, d, $J$ = 8.0 Hz, ArH), 7.11 (4 H, d, $J$ = 8.0 Hz, ArH), 6.97 (2 H, d, $J$ = 9.1 Hz, ArH), 4.77 (4 H, t, $J$ = 6.4 Hz, $CH_2CH_2$), 4.05 (4 H, t, $J$ = 6.3 Hz, $CH_2CH_2$), 2.55 (6 H, s, $ArCH_3$), 2.28 (6 H, s, $ArCH_3$); $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$: 159.2, 155.8, 150.5, 147.4, 145.6, 144.4, 143.9, 137.7, 128.1, 128.1, 125.5, 125.5, 125.0, 122.8, 112.3, 56.6, 49.2, 21.3, 20.7; HRMS (ESI): $m/z$ $[M + OTs]^+$ calcd for $C_{35}H_{37}N_6O_5S$: 653.2546; found: 653.2555 $\Delta$ = 1.4 ppm (salt with only one OTs counterion).

**2-(3-Cyano-4-((*E*)-3-(1-(2-(ethyl(4-((*E*)-(4-nitrophenyl)-diazenyl)phenyl)amino)ethyl)pyridin-4(1*H*)-ylidene)prop-1-enyl)-5,5-dioctylfuran-2(5*H*)-ylidene)malononitrile (MC1).** Compound **5** (0.67 g, 1.18 mmol) and TCF **7** (0.50 g, 0.99 mmol) were dissolved in anhydrous DCM (5 mL) under $N_2$. Triethylamine (0.3 mL, 2.17 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. The resulting solution was diluted with DCM (20 mL) and washed with brine (20 mL) and water (2 × 20 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was then dissolved in the minimum amount of DCM, and diethyl ether was added until a precipitate formed. The resulting dark blue solid was filtered and purified by column chromatography on silica (1:9 acetone/DCM) to give **MC1** (0.20 g, 26%) as a dark blue powder: mp 224−226 °C; $\lambda_{max}$ ($CHCl_3$) 647 $\log_{10}\varepsilon$ 5.19, (1,4-dioxane) 647 $\log_{10}\varepsilon$ 5.08, (DMF) 590 $\log_{10}\varepsilon$ 4.95, (MeOH) 588 $\log_{10}\varepsilon$ 4.85, (THF) 629 $\log_{10}\varepsilon$ 5.17; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.63 (1 H, t, $J$ = 13.3 Hz, CH═CH═CH), 8.33 (2 H, d, $J$ = 9.0 Hz, ArH), 7.95−7.92 (4 H, m, ArH), 7.66 (2 H, d, $J$ = 6.6 Hz, CH (pyridine ring)), 7.15 (2 H, d, $J$ = 6.2 Hz, CH (pyridine ring)), 6.77 (2 H, d, $J$ = 9.2 Hz, ArH), 5.90 (1 H, d, $J$ = 14.0 Hz, CH═CH═CH), 5.41 (1 H, d, $J$ = 12.7 Hz, CH═CH═CH), 4.48 (2 H, t, $J$ = 4.8 Hz, $NCH_2CH_2N$), 3.93 (2 H, t, $J$ = 4.8 Hz, $NCH_2CH_2N$), 3.30 (2 H, m, $J$ = 6.9 Hz, $NCH_2CH_3$), 1.89−1.82 (2 H, m, $CH_2$ ($C_8$ chain)), 1.60−1.49 (2 H, m, $CH_2$ ($C_8$ chain)), 1.32−1.17 (24 H, m, $CH_2$ ($C_8$ chain)), 1.15 (3 H, t, $J$ = 7.0 Hz, $NCH_2CH_3$), 0.86 (6 H, t, $J$ = 7.0 Hz, $CH_3$ ($C_8$ chain); $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 0.8:1; 8.52 (1.2 H, d, $J$ = 7.0 Hz, CH (pyridine ring)), 8.43−8.34 (3.4 H, m, 2H ArH, 0.8H CH (pyridine ring), 0.6 H CH═CH═CH), 7.96−7.91 (2 H, m, ArH), 7.83−7.80 (2.8 H, m, 2H ArH, 0.8H CH (pyridine ring)), 7.60 (0.4 H, dd, $J$ = 14.2, 12.8 Hz, CH═CH═CH), 7.47 (1.2 H, d, $J$ = 7.1 Hz, CH (pyridine ring)), 6.90 (2 H, d, $J$ = 9.2 Hz, ArH), 6.30 (0.4 H, d, $J$ = 14.3 Hz, CH═CH═CH), 6.22 (0.6 H, d, $J$ = 14.6 Hz, CH═CH═CH), 5.84 (0.4 H, d, $J$ = 12.5 Hz, CH═CH═CH), 5.59 (0.6 H, d, $J$ = 12.2 Hz, CH═CH═CH), 4.55 (1 H, q, $J$ = 5.8 Hz, $NCH_2CH_2N$), 3.97 (1 H, q, $J$ = 6.0 Hz, $NCH_2CH_2N$), 3.45−3.37 (1 H, m, $NCH_2CH_3$), 2.13−2.02 (0.8 H, m, $CH_2$ ($C_8$ chain)), 1.97−1.87 (0.8 H, m, $CH_2$ ($C_8$ chain)), 1.82−1.73 (1.2 H, m, $CH_2$ ($C_8$ chain)), 1.66−1.57 (1.2 H, m, $CH_2$ ($C_8$ chain)), 1.28−1.01 (27 H, m, $CH_2$ ($C_8$ chain), $NCH_2CH_3$), 0.82 (3.4 H, t, $J$ = 7.0 Hz, $CH_3$ ($C_8$ chain)), 0.79 (2.6 H, t, $J$ = 6.9 Hz, $CH_3$ ($C_8$ chain)); $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 0.8:1, 177.3, 175.7, 158.2, 157.5, 156.1, 153.5, 153.4, 151.1, 147.1, 147.1, 143.3, 142.7, 138.6, 138.0, 125.9, 125.0, 124.9, 122.6, 120.9, 120.1, 117.8, 117.0, 116.7, 114.8, 111.9, 111.8, 104.9, 103.5, 97.9, 97.5, 77.3, 73.7, 56.0, 55.8, 49.7, 49.4, 44.6, 44.5, 38.0, 37.7, 31.1, 28.8, 28.6, 28.5, 28.5, 28.4, 28.4, 22.1, 22.0, 13.9, 11.7, 11.7; HRMS (ESI): $m/z$ $[M + Na]^+$ calcd for $C_{48}H_{58}N_8O_3Na$: 817.4530; found: 817.4532 $\Delta$ = 0.2 ppm.

**2,2′-(4,4′-(1*E*,1′*E*)-3,3′-(1,1′-(2,2′-(4-((*E*)-(4-Nitrophenyl)-diazenyl)phenylazanediyl)bis(ethane-2,1-diyl))bis(pyridin-1(1*H*)-yl-4(1*H*)-ylidene))bis(prop-1-ene-1-yl-3-ylidene)bis(3-cyano-5,5-dioctylfuran-4(5*H*)-yl-2(5*H*)-ylidene))dimalononitrile (MC2).** Compound **6** (0.75 g, 0.91 mmol) and **7** (1.8 g, 3.6 mmol) were dissolved in anhydrous DCM (10 mL) under $N_2$. Triethylamine (0.5 mL, 3.6 mmol) was added, and the reaction mixture was stirred at room temperature for 48 h. The resulting solution was diluted with DCM (20 mL) and washed with brine (20 mL) and water (2 × 20 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting dark blue solid was filtered and purified by column chromatography on silica (1:9 → 1:1 acetone/DCM) to give **MC2** (0.4 g, 34%) as a dark blue powder: mp 186−188 °C; $\lambda_{max}$ ($CHCl_3$) 563 $\log_{10}\varepsilon$ 5.00, (1,4-dioxane) 520 $\log_{10}\varepsilon$ 4.78, (DMF) 591 $\log_{10}\varepsilon$ 5.12, (MeOH) 592 $\log_{10}\varepsilon$ 5.05, (THF) 636 $\log_{10}\varepsilon$ 4.97; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 0.65:1, 8.47−8.44 (2.4 H, m, CH (pyridine ring)), 8.42−8.32 (4.8 H, m, 2 H ArH, 1.6 H CH (pyridine ring), 1.2 H CH═CH═CH), 7.98−7.90 (2 H, m, ArH), 7.78 (3.6 H, d, $J$ = 9.0 Hz, 2H ArH, 1.6 H CH (pyridine ring)), 7.59 (0.8 H, dd, $J$ = 13.5, 13.5 Hz, CH═CH═CH), 7.48−7.40 (2.4 H, m, CH (pyridine ring), 6.98 (2 H, d, $J$ = 7.59 Hz, ArH), 6.28 (0.8 H, d, $J$ = 14.2 Hz, CH═CH═CH), 6.21 (1.2 H,


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d, $J$ = 14.6 Hz, C**H**=CH=CH), 5.83 (0.8 H, d, $J$ = 12.5 Hz, CH=CH=C**H**), 5.58 (1.2 H, d, $J$ = 12.2 Hz, CH=CH=C**H**), 4.54−4.48 (4 H, m, NC**H**$_2$CH$_2$N) 3.95−3.87 (4 H, m, NCH$_2$C**H**$_2$N), 2.11−2.00 (1.6 H, m, C**H**$_2$ (C$_8$ chain)), 1.97−1.87 (1.6 H, m, C**H**$_2$ (C$_8$ chain)), 1.82−1.71 (2.4H, m, C**H**$_2$ (C$_8$ chain)), 1.66−1.55 (2.4 H, m, C**H**$_2$ (C$_8$ chain)), 1.28−1.00 (48 H, m, C**H**$_2$ (C$_8$ chain)), 0.85−0.75 (12 H, m, C**H**$_3$ (C$_8$ chain)); $^1$H NMR (500 MHz, dichloromethane-$d_2$) $\delta$: 8.53−8.45 (2 H, m, CH=C**H**=CH), 8.32 (2 H, d, $J$ = 8.6 Hz, Ar**H**), 8.05 (2 H, d, $J$ = 8.5 Hz, Ar**H**), 7.97 (2 H, d, $J$ = 8.4 Hz, Ar**H**), 7.90 (4 H, br s, C**H** (pyridine ring)), 7.24 (4 H, br s, C**H** (pyridine ring)), 7.06 (2 H, d, $J$ = 8.3 Hz, Ar**H**), 5.89 (2 H, d, $J$ = 13.9 Hz, C**H**=CH=CH), 5.42−5.34 (2 H, m, CH=CH=C**H**, obscured by dichloromethane-$d_2$ solvent peak), 4.50 (4 H, br s, NC**H**$_2$CH$_2$N), 4.03−3.92 (4 H, m, NCH$_2$C**H**$_2$N), 1.93−1.85 (4 H, m, C**H**$_2$ (C$_8$ chain)), 1.67−1.51 (4 H, m, C**H**$_2$ (C$_8$ chain), obscured by water peak), 1.38−1.13 (48 H, m, C**H**$_2$ (C$_8$ chain)), 0.87 (12 H, t, $J$ = 6.7 Hz, C**H**$_3$ (C$_8$ chain)); $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 0.65:1, 177.3, 175.7, 157.6, 155.8, 153.5, 153.4, 150.3, 147.3, 147.3, 143.8, 143.1, 142.6, 138.7, 138.0, 125.6, 124.9, 122.8, 120.7, 120.0, 117.7, 116.9, 116.6, 116.5, 116.2, 114.7, 112.3, 104.9, 103.4, 97.9, 97.5, 77.4, 73.7, 55.4, 55.1, 49.6, 49.4, 38.1, 37.8, 31.1, 28.7, 28.6, 28.4, 28.3, 22.0, 13.9; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{80}H_{98}N_{12}O_4Na$: 1313.7732; found: 1313.7725 $\Delta$ = 0.5 ppm.

**3-Hydroxy-3-octylundecan-2-one (9).** In a 250 mL round-bottom flask were placed dry diethyl ether (20 mL) and magnesium turnings (2.64 g, 110 mmol). A solution of 1-bromooctane (21.2 g, 110 mmol) in diethyl ether (100 mL) was placed in a dropping funnel. A few drops of the halide were then added to the magnesium turnings in order to initiate the reaction, after which the halide was added at such a rate as to maintain a steady reflux. In some instances, it was necessary to add a small crystal of iodine to initiate the reaction. After all the halide was added, the reaction mixture was held at reflux for a further 15 min. The mixture was allowed to cool, and ethyl 2,2-diethoxypropanoate (**8**)[40] (9.5 g, 50 mmol) was added dropwise and the solution refluxed for a further 2 h. The reaction mixture was quenched by adding it in small portions to 20:1 $H_2O$/HCl (200 mL) and then stirred for a further 2 h. The solution was then concentrated in vacuo to afford a yellow solid to which was added ethanol/$H_2O$/HCl (4:4:1; 300 mL) and the solution refluxed for 2 h. The solvent was removed in vacuo, and the residue was extracted into dichloromethane (4 × 50 mL). The organic phase was then washed with water (3 × 100 mL), dried ($MgSO_4$), and then concentrated in vacuo to give the product **9** as a pale yellow oil (12.4 g, 83%). The crude product was found to be suitable for use without further purification: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 4.73 (1H, s, O**H**), (2.10 (3H, s, C**H**$_3$CO), 1.62−1.53 (2H, m, C**H**$_2$), 1.49−1.38 (2H, m, C**H**$_2$), 1.36−1.12 (22H, m, 11 × C**H**$_2$), 1.04−0.94 (2H, m, C**H**$_2$), 0.85 (6H, t, $J$ = 7.0 Hz, CH$_2$C**H**$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 212.2, 81.7, 38.9, 31.8, 29.9, 29.4, 29.2, 23.8, 23.2, 22.6, 14.0; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{19}H_{38}O_2Na$: 321.2770; found: 321.2773 $\Delta$ = 0.9 ppm.

**3-Hydroxy-3-undecyltetradecan-2-one (10).** In a 250 mL round-bottom flask were placed dry diethyl ether (20 mL) and magnesium turnings (2.45 g, 102 mmol). A solution of 1-bromoundecane (24.0 g, 102 mmol) in diethyl ether THF (100 mL) was placed in a dropping funnel. A few drops of the halide were then added to the magnesium turnings in order initiate the reaction, after which the halide was added at such a rate as to maintain a steady reflux. In some instances, it was necessary to add a small crystal of iodine to initiate the reaction. After all the halide was added, the reaction mixture was held at reflux for a further 15 min. The mixture was allowed to cool, and ethyl 2,2-diethoxypropanoate (**8**)[40] (9.5 g, 50 mmol) was added dropwise and the solution refluxed for a further 2 h. The reaction mixture was quenched by adding it in small portions to 20:1 $H_2O$/HCl (200 mL) and then stirred for a further 2 h. The solution was then concentrated in vacuo to afford a yellow solid to which was added ethanol/$H_2O$/HCl (4:4:1; 300 mL) and the solution refluxed for 2 h. The solvent was removed in vacuo, and the residue was extracted into dichloromethane (4 × 50 mL). The organic phase was then washed with water (3 × 100 mL), dried ($MgSO_4$), and then concentrated in vacuo to give the product **10** as a white solid (13.68 g, 72%). The crude product was found to be suitable for use without further purification. An analytical sample was prepared by recrystallization from isopropyl alcohol, to afford colorless needles: mp 36−37 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.82 (1H, s, O**H**), 2.17 (3H, s, C**H**$_3$CO), 1.70−1.65 (4H, m, C**H**$_2$), 1.32−1.22 (36H, m, C**H**$_2$), 0.88 (6H, t, $J$ = 7.0 Hz, CH$_2$C**H**$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 212.4, 81.8, 38.9, 31.9, 29.9, 29.7, 29.6, 29.6, 29.5, 29.3, 23.9, 23.2, 22.7, 14.1; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{25}H_{50}O_2Na$: 405.3709; found: 405.3705 $\Delta$ = 1.0 ppm.

**2-(3-Cyano-4-methyl-5,5-dioctylfuran-2(5*H*)-ylidene)-malononitrile (11).** In a round-bottom flask were added **9** (12.4 g, 41.6 mmol), malononitrile (11.0 g, 166 mmol), acetic acid (0.13 mL, 2.03 mmol), ammonium acetate (39 mg, 0.41 mmol), and pyridine (160 mL). The reaction was then stirred for 10 days at room temperature and for 4 days at 40 °C until the reaction was deemed complete by TLC. The solution was concentrated in vacuo, water (120 mL) was added, and the mixture was again concentrated in vacuo. The residue was then suspended in 4:1 $H_2O$/EtOH (200 mL). The resulting solid was collected by filtration and washed thoroughly with cold water (3 × 40 mL). The solid was suspended in 3:1 $H_2O$/IPA (120 mL) at 40 °C with vigorous stirring for an hour. The solid was then filtered and washed with IPA (2 × 20 mL) to give the product **11** as a cream solid (12.0 g, 77%): mp 71−72 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.28 (3H, s, CC**H**$_3$), 2.04 (2H, ddd, $J$ = 14.7, 12.2, 4.4 Hz, C**H**$_2$), 1.75 (2H, ddd, $J$ = 14.7, 11.9, 4.6 Hz, C**H**$_2$), 1.36−1.21 (20H, m, C**H**$_2$), 1.20−1.11 (2H, m, C**H**$_2$), 1.03−0.91 (2H, m, C**H**$_2$), 0.89 (6H, t, $J$ = 7.0 Hz, CH$_2$C**H**$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 181.7, 176.0, 111.0, 110.5, 108.9, 106.3, 105.1, 57.7, 36.8, 31.7, 29.2, 29.1, 29.0, 22.6, 22.6, 14.5, 14.0; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{25}H_{37}N_3ONa$: 418.2834; found: 418.2832 $\Delta$ = 0.5 ppm.

**2-(3-Cyano-4-methyl-5,5-diundecylfuran-2(5*H*)-ylidene)-malononitrile (12).** In a round-bottom flask were added **10** (10.55 g, 27.6 mmol), malononitrile (7.26 g, 110 mmol), acetic acid (81 mg, 1.35 mmol), ammonium acetate (21 mg, 0.27 mmol), and pyridine (125 mL). The reaction was then stirred for 72 h at room temperature until the reaction was deemed complete by TLC. The pyridine was then removed under reduced pressure until ca. 100 mL remained, water (200 mL) was added, and the mixture was again reduced to ca. 100 mL in volume. The dilution/evaporation procedure was repeated three times in total, after which a solid had formed. This was collected by filtration and washed thoroughly with cold water to remove all traces of pyridine, and then with ethanol (2 × 5 mL) to give the target acceptor **12** dark red crystals (10.3 g, 78%). An analytical sample was obtained via recrystallization from isopropyl alcohol to afford light pink flakes: mp 249−250 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.28 (3H, s, CC**H**$_3$), 2.07−2.00 (2H, m, C**H**$_2$), 1.78−1.71 (2H, m, C**H**$_2$), 1.33−1.21 (36H, m, C**H**$_2$), 0.90−0.86 (6H, m, CH$_2$C**H**$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 181.6, 176.0, 111.0, 110.5, 108.9, 106.4, 105.1, 58.0, 36.9, 31.9, 31.9, 29.7, 29.5, 29.4, 29.4, 29.3, 29.2, 22.7, 14.5, 14.1; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{31}H_{49}ON_3Na$: 502.3773 found: 502.3774 $\Delta$ = 0.2 ppm.

**(*E*)-*N*-(2-(4-Cyano-5-(dicyanomethylene)-2,2-dioctyl-2,5-dihydrofuran-3-yl)vinyl)-*N*-phenylacetamide (7).** A mixture of *N*,*N*′-diphenylformamidine (1.5 g, 7.64 mmol) and **11** (3 g, 7.58 mmol) in acetic anhydride (15 mL) were stirred at 80 °C for 24 h. The solvent was removed under reduced pressure to give the crude product as a green oil. The crude product was purified by column chromatography on silica (0:1 → 1:9 acetone/dichloromethane) to give the product **7** as a yellow solid (3.20 g, 78%): mp 69−71 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.76 (1 H, d, $J$ = 14.5 Hz, C**H**=CH), 7.65−7.57 (3 H, m, Ar**H**), 7.23 (2 H, m, Ar**H**), 5.28 (1 H, d, $J$ = 14.5 Hz, CH=C**H**), 2.12−2.05 (2 H, m, C**H**$_2$), 2.04 (3 H, s, COC**H**$_3$), 1.87−1.79 (2 H, m, C**H**$_2$), 1.34−1.19 (20 H, m, C**H**$_2$), 1.17−1.06 (2 H, m, C**H**$_2$), 1.04−0.93 (2 H, m, C**H**$_2$), 0.88 (6 H, t, $J$ = 7.0 Hz, CH$_2$C**H**$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 176.7, 174.0, 169.8, 142.6, 136.4, 131.1, 130.7, 127.8, 112.0, 111.4, 110.1, 102.9,100.1, 98.2, 55.0, 39.2, 31.7, 29.1, 29.1, 29.0, 23.3, 22.6, 22.6, 14.1; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{34}H_{44}N_4O_2Na$: 563.3362; found: 563.3367 $\Delta$ = 0.9 ppm.


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**3-(Pyridin-4-yl)propyl octanoate (14).** Octanoic acid (9.7 mL, 61 mmol) and 4-pyridinepropanol (**13**) (10 g, 73 mmol) were dissolved in anhydrous dichloromethane (200 mL). EDCI (14 g, 73 mmol) and DMAP (9 g, 73 mmol) were added, and the reaction mixture was stirred at rt for 18 h. The reaction mixture was then washed sequentially with 0.5 M aqueous HCl (200 mL), saturated aqueous $NaHCO_3$ (200 mL), and saturated aqueous NaCl (200 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo to give a pale yellow oil. The crude product was purified by column chromatography on silica (2:3 ethyl acetate/petroleum spirits) to give **14** (15 g, 96%) as a colorless oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.54 (2 H, d, $J$ = 6.1 Hz, Ar**H**), 7.19 (2 H, d, $J$ = 6.1 Hz, Ar**H**), 4.13 (2 H, t, $J$ = 6.4 Hz, C**H**$_2$O), 2.76−2.72 (2 H, m, C**H**$_2$CH$_2$CH$_2$O), 2.32 (2 H, t, $J$ = 7.5 Hz, C(=O)C**H**$_2$), 2.05−1.98 (2 H, m, CH$_2$C**H**$_2$CH$_2$O), 1.68−1.62 (2 H, m, C(=O)CH$_2$C**H**$_2$), 1.38−1.27 (8 H, m, (C**H**$_2$)$_4$CH$_3$), 0.91 (3 H, t, $J$ = 7.0 Hz, C**H**$_3$); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 173.6, 150.2, 149.6, 123.7, 63.0, 34.1, 31.6, 31.5, 29.1, 29.0, 28.8, 24.9, 22.5, 13.9; HRMS (ESI): $m/z$ [M + H]$^+$ calcd for $C_{16}H_{26}NO_2$: 264.1964; found: 264.1966 Δ = 0.8 ppm.

**(*E*)-5-(4-Cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)-3-(1-(2-(ethyl(4-((*E*)-(4-nitrophenyl)diazenyl)phenyl)amino)ethyl)pyridin-4(1*H*)-ylidene)pent-4-enyl Octanoate (MC3).** Compounds **3** (1.47 g, 3.13 mmol) and **14** (1.65 g, 6.26 mmol) were dissolved in ethanol (15 mL) and refluxed for 16 h. The solution was concentrated in vacuo and triturated with diethyl ether and allowed to stand, whereupon a red solid formed. This solid was collected by filtration and washed with diethyl ether (3 × 20 mL) to give (*E*)-1-(2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)-ethyl)-4-(3-(octanoyloxy)propyl)pyridinium 4-methylbenzenesulfonate as a red solid (1.69 g, 74%), which was used without further purification. Selected data: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 9.13 (2 H, d, $J$ = 6.5 Hz, Ar**H**), 8.35 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 7.93 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 7.83 (2 H, d, $J$ = 8.1 Hz, Ar**H**), 7.79 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 7.68 (1 H, d, $J$ = 6.5 Hz, Ar**H**), 7.21 (1 H, d, $J$ = 7.9 Hz, Ar**H**), 6.67 (1 H, d, $J$ = 9.1 Hz, Ar**H**), 5.21 (2 H, t, $J$ = 5.5 Hz, NC**H**$_2$CH$_2$N), 4.15 (2 H, t, $J$ = 5.6 Hz, NCH$_2$C**H**$_2$N), 4.02 (2 H, t, $J$ = 6.2 Hz, C**H**$_2$O), 3.41 (1 H, q, $J$ = 7.0 Hz, NC**H**$_2$CH$_3$), 2.88−2.83 (2 H, m, C**H**$_2$CH$_2$O), 2.38 (3 H, s, ArC**H**$_3$), 2.30 (2 H, t, $J$ = 7.6 Hz, C(=O)C**H**$_2$), 1.96−1.89 (2 H, m, CH$_2$C**H**$_2$CH$_2$O), 1.66−1.58 (2 H, m, C(=O)CH$_2$C**H**$_2$), 1.38−1.26 (8 H, m, (C**H**$_2$)$_4$CH$_3$),), 1.10 (3 H, t, $J$ = 7.0 Hz, NCH$_2$C**H**$_3$), 0.91 (3 H, t, $J$ = 7.0 Hz, (CH$_2$)$_6$C**H**$_3$); HRMS (ESI): $m/z$ [M]$^+$ calcd for $C_{32}H_{42}N_5O_4$: 560.3237; found: 560.3237 Δ = 0.0 ppm.

(*E*)-1-(2-(Ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl)-4-(3-(octanoyloxy)propyl)pyridinium 4-methylbenzenesulfonate (1.69 g, 2.31 mmol) and **15** (0.63 g, 1.93 mmol) were dissolved in methanol (15 mL). Triethylamine (0.3 mL, 2.3 mmol) was added and the reaction mixture refluxed for 40 h. After the mixture was cooled down to room temperature, the precipitate was filtered and washed with diethyl ether (20 mL). The crude product was then recrystallized from DCM and diethyl ether to give **MC3** (305 mg, 21%) as a black powder: mp 214−216 °C; $\lambda_{max}$ ($CHCl_3$) 646 log$_{10}\varepsilon$ 5.02, (1,4-dioxane) 645 log$_{10}\varepsilon$ 4.99, (DMF) 590 4.75, (MeOH) 588 log$_{10}\varepsilon$ 4.74, (THF) 628 log$_{10}\varepsilon$ 4.98; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.67 (1 H, d, $J$ = 12.9 Hz, C**H**=CH), 8.36 (2 H, d, $J$ = 9.0 Hz, Ar**H**), 7.98−7.93 (4 H, m, Ar**H**), 7.76 (2 H, d, $J$ = 6.8 Hz, C**H** (pyridine ring)), 7.47 (2 H, d, $J$ = 6.8 Hz, C**H** (pyridine ring)), 6.77 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 5.63 (1 H, d, $J$ = 13.1 Hz, CH=C**H**), 4.50−4.45 (2 H, m, NC**H**$_2$CH$_2$N), 4.06−4.01 (2 H, m, CH$_2$C**H**$_2$O), 3.94 (2 H, t, $J$ = 5.3 Hz, NCH$_2$C**H**$_2$N), 3.35 (2 H, q, $J$ = 7.0 Hz, NC**H**$_2$CH$_3$), 2.83−2.74 (2 H, m, C**H**$_2$CH$_2$O), 2.33−2.29 (2 H, m, C(=O)C**H**$_2$), 1.68−1.56 (2 H, m, C(=O)CH$_2$C**H**$_2$), 1.54 (6 H, s, C(C**H**$_3$)$_2$), 1.36−1.28 (8 H, m, (C**H**$_2$)$_4$CH$_3$), 1.18 (3 H, t, $J$ = 7.0 Hz, NCH$_2$C**H**$_3$), 0.91 (3 H, t, $J$ = 6.9 Hz, (CH$_2$)$_6$C**H**$_3$); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 174.1, 156.4, 150.0, 147.9, 144.6, 140.7, 140.5 (2 × CH), 126.3, 124.7, 122.9, 118.9, 118.5, 116.6, 116.4, 115.9, 112.0, 100.5, 93.9, 61.2, 56.2, 50.8, 46.4, 43.5, 34.3, 31.6, 29.1, 28.9, 27.2, 26.2, 24.9, 22.6, 14.0, 12.0; HRMS (ESI): $m/z$ [M + H]$^+$ calcd for $C_{44}H_{49}N_8O_5$: 769.3826; found: 769.3828 Δ = 0.3 ppm.

**(*E*)-4-((4-(Ethyl(2-hydroxyethyl)amino)phenyl)diazenyl)-benzaldehyde (18).** To conc. sulfuric acid (11 mL) was added *p*-aminobenzaldehyde (**16**) (6.23 g, 51.4 mmol) and the solution cooled to 0 °C. A solution of $NaNO_2$ dissolved in cold water (7 mL) was added slowly to this solution with stirring, and the reaction was maintained at 0−5 °C for 30 min. To this mixture, a solution of *N*-ethyl-*N*-(2-hydroxyethyl)aniline (**17**) (7.08 g, 42.9 mmol) in glacial acetic acid (39 mL) was added dropwise at 0−5 °C. Sodium acetate (1.78 g, 21.6 mmol) was then added, the mixture was stirred for a further 2 h and then poured into water (100 mL) and neutralized with aq. $Na_2CO_3$. The resulting precipitate was filtered and washed with water to give **18** (7.75 g, 61%) as a dark red solid. Spectral properties are in agreement with the literature:[48,49] mp 107−109 °C (lit. 108−110 °C);[48] $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 10.06 (1 H, s, C**H**O), 7.99 (1 H, d, $J$ = 8.5 Hz, Ar**H**), 7.94 (1 H, d, $J$ = 8.5 Hz, Ar**H**), 7.90 (1 H, d, $J$ = 9.2 Hz, Ar**H**), 6.80 (1 H, d, $J$ = 9.2 Hz, Ar**H**), 4.29 (1 H, t, $J$ = 6.3, 6.3 Hz), 3.68 (1 H, t, $J$ = 6.3 Hz), 1.26 (1 H, t, $J$ = 7.1 Hz), 3.53 (1 H, dd, $J$ = 13.5, 6.4 Hz).

**2-(3-Cyano-4-(4-((*E*)-(4-(ethyl(2-hydroxyethyl)amino)-phenyl)diazenyl)styryl)-5,5-diundecylfuran-2(5*H*)-ylidene)-malononitrile (19).** A mixture of **18** (4.0 g, 13.5 mmol), **12** (6.78 g, 14.1 mmol), and triethylamine (cat. amount) in 80 mL of methanol was refluxed for 16 h. The solution was concentrated in vacuo to give a purple oil, which was purified by column chromatography on silica (1:19 ethyl acetate/DCM) to give **19** (4.0 g, 39%) as a dark purple solid: mp 146−147 °C; $\lambda_{max}$ ($CHCl_3$) 564 log$_{10}\varepsilon$ 4.63, (1,4-dioxane) 546 log$_{10}\varepsilon$ 4.65, (DMF) 336/436 log$_{10}\varepsilon$ 4.52/4.30, (MeOH) 551 log$_{10}\varepsilon$ 4.60, (THF) 556 log$_{10}\varepsilon$ 4.66; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.92 (2 H, d, $J$ = 8.6 Hz, Ar**H**), 7.89 (2 H, d, $J$ = 9.2 Hz, Ar**H**), 7.73 (2 H, d, $J$ = 8.6 Hz, Ar**H**), 7.68 (1 H, d, $J$ = 16.4 Hz, C**H**=CH), 7.05 (1 H, d, $J$ = 16.3 Hz, CH=C**H**), 6.82 (2 H, d, $J$ = 9.3 Hz, Ar**H**), 3.92−3.87 (2 H, m, NCH$_2$C**H**$_2$OH), 3.62 (2 H, t, $J$ = 5.9 Hz, NCH$_2$C**H**$_2$OH), 3.57 (2 H, q, $J$ = 7.1 Hz, NC**H**$_2$CH$_3$), 2.18 (2 H, ddd, $J$ = 14.6, 12.0, 4.1 Hz, CH$_2$ (C$_{11}$ chain)), 1.96 (2 H, ddd, $J$ = 15.0, 11.6, 4.5 Hz, CH$_2$ (C$_{11}$ chain)), 1.33−1.15 (34 H, m, CH$_2$ (C$_{11}$ chain)), 1.26 (3 H, t, $J$ = 7.1 Hz, NCH$_2$C**H**$_3$) 1.14−1.01 (2 H, m, CH$_2$ (C$_{11}$ chain)), 0.86 (6 H, t, $J$ = 7.0 Hz, CH$_3$ (C$_{11}$ chain)); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 176.2, 172.1, 155.8, 151.5, 145.8, 144.0, 134.1, 130.1, 126.1, 123.3, 115.1, 111.7, 111.0, 110.2, 103.4, 101.5, 60.3, 57.1, 52.4, 46.0, 38.9, 31.9, 29.5, 29.4, 29.3, 29.2, 29.2, 22.7, 22.7, 14.1, 12.1; HRMS (ESI): $m/z$ [M + H]$^+$ calcd for $C_{48}H_{67}N_6O_2$: 759.5326; found: 759.5319 Δ = 0.9 ppm.

**2-((4-((*E*)-(4-((*E*)-2-(4-Cyano-5-(dicyanomethylene)-2,2-diundecyl-2,5-dihydrofuran-3-yl)vinyl)phenyl)diazenyl)phenyl)-(ethyl)amino)ethyl 3-((*E*)-4-((*E*)-3-(4-Cyano-5-(dicyanomethylene)-2,2-dioctyl-2,5-dihydrofuran-3-yl)allylidene)-quinolin-1(4*H*)-yl)propanoate (MC4).** To a solution of **19** (0.56 g, 0.74 mmol) and **20** (0.69 g, 1.11 mmol) in 10 mL of anhydrous DCM under $N_2$ was added EDCI (0.28 g, 1.48 mmol) and DMAP (catalytic amount). The resultant mixture was stirred at rt overnight. The solution was then diluted with DCM (50 mL) and washed with brine (50 mL) and water (50 mL). The organic phase was dried over $Na_2SO_4$, and the solvent was concentrated in vacuo. The residue was purified by column chromatography on silica (1:9 ethyl acetate: DCM) to give **MC4** (211 mg, 21%) as a dark green solid: mp 110−112 °C; $\lambda_{max}$ ($CHCl_3$) 701 log$_{10}\varepsilon$ 5.21, (1,4-dioxane) 703 log$_{10}\varepsilon$ 5.10, (DMF) 668 log$_{10}\varepsilon$ 5.05, (MeOH) 665 log$_{10}\varepsilon$ 4.93, (THF) 695 log$_{10}\varepsilon$ 5.16; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.81 (1 H, br s, CH=C**H**=CH), 8.09 (1 H, d, $J$ = 8.2 Hz, C**H**(quinoline)), 7.84 (2 H, d, $J$ = 8.5 Hz, Ar**H**), 7.75−7.65 (7 H, m, 2 × Ar**H**, CC**H**=CHC, 2 × C**H**(quinoline)), 7.46−7.39 (2 H, m, 2 × C**H**(quinoline)), 7.08−6.99 (1 H, m, C**H**(quinoline)) 7.02 (1 H, d, $J$ = 16.3 Hz, CCH=C**H**C), 6.66 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 6.56 (1 H, d, $J$ = 13.3 Hz, C**H**=CH=CH), 5.63 (1 H, br s, CH=CH=C**H**), 4.47 (2 H, t, $J$ = 6.0 Hz, C(=O)CH$_2$C**H**$_2$N), 4.30 (2 H, t, $J$ = 5.8 Hz, NC**H**$_2$CH$_2$O), 3.59 (2 H, t, $J$ = 5.7 Hz, NCH$_2$C**H**$_2$O), 3.37 (2 H, q, $J$ = 7.0 Hz, NC**H**$_2$CH$_3$), 2.84 (2 H, t, $J$ = 6.2 Hz, C(=O)C**H**$_2$CH$_2$N), 2.17−2.08 (2 H, m, CH$_2$ (alkyl chains)), 1.98−1.80 (4 H, m, CH$_2$ (alkyl chains)), 1.67−1.52 (2 H, m, CH$_2$ (alkyl chains)), 1.29−0.95 (63 H, m, CH$_2$ (alkyl chains), NCH$_2$C**H**$_3$), 0.82−0.73 (12 H, m, CH$_3$ (alkyl chains)); $^{13}$C NMR


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(126 MHz, $CDCl_3$) $\delta$: 178.8, 176.2, 172.4, 170.1, 167.2, 155.5, 151.0, 150.4, 145.8, 144.2, 144.0, 140.9, 137.7, 134.4, 133.3, 130.2, 126.1, 125.9, 125.6, 124.8, 123.3, 116.6, 115.9, 115.3, 114.9, 111.6, 111.4, 111.1, 110.3, 110.0, 109.0, 106.5, 103.6, 101.3, 99.9, 62.3, 56.9, 49.5, 48.4, 46.4, 45.2, 39.3, 38.8, 33.0, 31.8, 31.8, 31.7, 29.5, 29.4, 29.3, 29.3, 29.2, 29.0, 22.7, 22.6, 22.6, 14.0, 12.1; HRMS (ESI): $m/z$ $[M + H]^+$ calcd for $C_{87}H_{113}N_{10}O_4$: 1361.8938; found: 1361.8946 $\Delta$ = 0.6 ppm.

**3-((*Z*)-4-((*E*)-3-(4-Cyano-5-(dicyanomethylene)-2,2-dioctyl-2,5-dihydrofuran-3-yl)allylidene)quinolin-1(4*H*)-yl)propanoic Acid (20).** 1-(2-Carboxyethyl)-4-methylquinolinium bromide (**21**) (1.40 g, 4.73 mmol) and TCF derivative **7** (2.00 g, 3.94 mmol) were dissolved in anhydrous DCM (20 mL) under $N_2$. Triethylamine (1.2 mL, 8.67 mmol) was added, and the reaction mixture was stirred at room temperature for 48 h. The resulting solution was then concentrated in vacuo. The resulting residue was then dissolved in 10% NaOH and filtered to remove any insoluble material. The filtrate was then cooled in an ice bath and conc. HCl was added dropwise until the pH = 7. The resulting precipitate was filtered and washed with water (100 mL). The resulting dark blue oily solid was purified by column chromatography on silica (0:1 → 1:9 methanol/ethyl acetate) to give **20** (1.28 g, 52%) as a dark blue solid: mp 222−223 °C; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two isomers approximately 1:1, 8.86 (0.5H, d, $J$ = 6.9 Hz, CH (pyridine ring)), 8.74−8.66 (1.5H, m, CH═C**H**═CH, CH (pyridine ring), ArH), 8.57 (0.5H, d, $J$ = 8.7 Hz, ArH), 8.23 (0.5H, d, $J$ = 8.8 Hz, ArH), 8.19 (0.5H, d, $J$ = 8.8 Hz, ArH), 8.09 (0.5H, d, $J$ = 7.1 Hz, CH (pyridine ring)), 8.07−7.99 (1H, m, 2 × ArH), 7.88 (0.5H, t, $J$ = 13.2 Hz, CH═C**H**═CH), 7.80 (0.5H, dd, $J$ = 7.7, 7.7 Hz, ArH), 7.75 (0.5H, dd, $J$ = 7.7, 7.7 Hz, ArH), 7.42 (0.5H, d, $J$ = 6.9 Hz, ArH (pyridine ring)), 7.29 (0.5H, d, $J$ = 13.8 Hz, C**H**═CH═CH), 7.18 (0.5H, d, $J$ = 14.0 Hz, CH═CH═C**H**), 6.24 (0.5H, d, $J$ = 12.7 Hz, CH═CH═C**H**), 5.88 (0.5H, d, $J$ = 12.3 Hz, C**H**═CH═CH), 4.83 (2H, t, $J$ = 6.4 Hz, C**H**$_2$CH$_2$CO$_2$H), 2.59−2.53 (2H, m, CH$_2$C**H**$_2$CO$_2$H), 2.20−2.12 (1H, m, CH$_2$ ($C_8$ chain)), 2.03−1.94 (1H, m, CH$_2$ ($C_8$ chain)), 1.90−1.82 (1H, m, CH$_2$ ($C_8$ chain)), 1.72−1.65 (1H, m, CH$_2$ ($C_8$ chain)), 1.29−1.07 (24H, m, CH$_2$ ($C_8$ chain)), 0.81 (3H, t, $J$ = 6.7, 6.7 Hz, CH$_3$ ($C_8$ chain)), 0.73 (3H, t, $J$ = 6.4, 6.4 Hz, CH$_3$ ($C_8$ chain)); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.65−8.49 (2 H, m, CH═C**H**═CH, CH (pyridine ring)), 8.16 (1 H, d, $J$ = 7.7 Hz, CH(quinoline)), 7.97−7.85 (2 H, m, 2 × CH(quinoline)), 7.63−7.54 (1 H, m, CH(quinoline)), 7.27 (1 H, br s, CH (pyridine ring)), 6.61 (1 H, d, $J$ = 12.7 Hz, C**H**═CH═CH), 5.51 (1 H, d, $J$ = 10.7 Hz, CH═CH═C**H**), 4.88 (2 H, br s, C**H**$_2$CH$_2$CO$_2$H), 3.06 (2 H, br s, CH$_2$C**H**$_2$CO$_2$H), 1.90−1.79 (2 H, m, CH$_2$ ($C_8$ chain)), 1.62−1.50 (2 H, m, CH$_2$ ($C_8$ chain)), 1.36−1.08 (24 H, m, CH$_2$ ($C_8$ chain)), 0.87 (6 H, t, $J$ = 6.7 Hz, CH$_3$ ($C_8$ chain)); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 178.3, 176.2, 163.1, 151.8, 144.3, 142.0, 138.3, 134.0, 127.1, 125.2, 125.0, 118.0, 117.8, 116.7, 115.8, 111.3, 110.9, 105.2, 98.7, 51.8, 42.4, 39.1, 35.1, 31.9, 29.8, 29.4, 22.7, 14.2; HRMS (ESI): $m/z$ $[M + H]^+$ calcd for $C_{39}H_{49}N_4O_3$: 621.3805; found: 621.3796 $\Delta$ = 1.5 ppm.

**2-(3-Cyano-4-((1*E*,3*E*)-3-(1-(2-hydroxyethyl)quinolin-4(1*H*)-ylidene)prop-1-enyl)-5,5-dioctylfuran-2(5*H*)-ylidene)malononitrile (23).** Compound **22** (1.86 g, 5.91 mmol) and **7** (2.5 g, 4.92 mmol) were dissolved in anhydrous DCM (10 mL) under $N_2$. Triethylamine (0.85 mL, 5.91 mmol) was added, and the reaction mixture was stirred at room temperature for 48 h. The resulting solution was diluted with DCM (20 mL) and washed with brine (20 mL) and water (2 × 20 mL). The organic phase was dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The resulting dark blue oil was purified by column chromatography on silica (0:1 → 3:7 acetone/DCM) to give **23** (581 mg, 20%) as a blue powder: mp 215−216 °C; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two isomers approximately 0.85:1, 8.77−8.67 (1.46 H, m, 0.46 H CH═C**H**═CH (minor), 0.54 H Ar**H** (quinoline) (major), 0.46 H CH (pyridine ring)(minor)), 8.59 (0.46 H, d, $J$ = 8.2 Hz, Ar**H** (quinoline)), 8.48 (0.54 H, d, $J$ = 7.0 Hz, C**H** (pyridine ring)), 8.27 (0.46 H, d, $J$ = 8.9 Hz, Ar**H** (quinoline)), 8.23 (0.54 H, d, $J$ = 8.8 Hz, Ar**H** (quinoline)), 8.10 (0.54 H, d, $J$ = 7.0 Hz, CH (pyridine ring)), 8.06−7.98 (1 H, m, 0.54 and 0.46 H Ar**H** (quinoline)), 7.91 (0.54 H, dd, $J$ = 13.3 Hz, CH═C**H**═CH), 7.83−7.79 (0.46 H, m, Ar**H** (quinoline)), 7.76 (0.54 H, t, $J$ = 7.8 Hz, Ar**H** (quinoline)), 7.48 (0.46 H, d, $J$ = 7.0 Hz, CH(pyridine ring)), 7.31 (0.54 H, d, $J$ = 13.7 Hz, C**H**═CH═CH), 7.21 (0.46 H, d, $J$ = 14.1 Hz, C**H**═CH═CH), 6.27 (0.54 H, d, $J$ = 12.8 Hz, CH═CH═C**H**), 5.90 (0.46 H, d, $J$ = 12.4 Hz, CH═CH═C**H**), 5.12−5.05 (1 H, m, NCH$_2$CH$_2$O**H**), 4.80−4.74 (2 H, m, NC**H**$_2$CH$_2$OH), 3.88−3.82 (2 H, m, NCH$_2$C**H**$_2$OH), 2.22−2.13 (1.08 H, m, CH$_2$ ($C_8$ chain)), 2.06−1.96 (1.08 H, m, CH$_2$ ($C_8$ chain)), 1.91−1.83 (0.92 H, m, CH$_2$ ($C_8$ chain)), 1.73−1.65 (0.92 H, m, CH$_2$ ($C_8$ chain)), 1.32−1.07 (24 H, m, CH$_2$ ($C_8$ chain)), 0.82 (2.76 H, t, $J$ = 6.7 Hz, CH$_3$ ($C_8$ chain)), 0.74 (3.24 H, t, $J$ = 6.7 Hz, CH$_3$ ($C_8$ chain)); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.62 (dd, $J$ = 13.0, 13.0 Hz, 1H, CH═C**H**═CH), 8.19 (d, $J$ = 8.3 Hz, 1H, ArH), 8.15 (d, $J$ = 6.0 Hz, 1H, ArH (pyridine ring)), 7.95 (dd, $J$ = 7.6, 7.6 Hz, 1H, ArH), 7.87 (d, $J$ = 8.5 Hz, 1H, ArH), 7.64 (dd (apparent triplet), $J$ = 7.7, 7.7 Hz, 1H, ArH), 7.32 (d, $J$ = 6.9 Hz, 1H, ArH (pyridine ring)), 6.66 (d, $J$ = 13.7 Hz, 1H, C**H**═CH═CH), 5.49 (d, $J$ = 12.5 Hz, 1H, CH═CH═C**H**), 4.64 (br s, 2H, C**H**$_2$CH$_2$(OH)), 4.15 (br s, 2H, CH$_2$C**H**$_2$(OH)), 3.74 (br s, 1H, O**H**), 1.90−1.82 (m, 2H, C**H**$_2$), 1.61−1.52 (m, 2H, C**H**$_2$), 1.35−1.12 (m, 30H, 15 × C**H**$_2$), 0.86 (t, $J$ = 6.8 Hz, 3H, C**H**$_3$); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 178.5, 163.7, 152.1, 143.3, 142.7, 138.5, 134.0, 126.9, 125.4, 124.9, 117.5, 117.4, 115.8, 111.0, 110.2, 105.2, 98.9, 77.7, 59.3, 57.3, 43.4, 39.5, 31.9, 29.7, 29.5, 29.3, 22.7, 22.6, 14.1; HRMS (ESI): $m/z$ $[M + Na]^+$ calcd for $C_{38}H_{48}N_4O_2Na$: 615.3675; found: 615.3677 $\Delta$ = 0.3 ppm.

**(*E*)-2-(3-Cyano-4-(4-((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethylfuran-2(5*H*)-ylidene)malononitrile (25a).** To a solution of 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde **24** (5.0 g, 28 mmol) and 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)-malononitrile (5.6 g, 28 mmol) in absolute ethanol (100 mL), a catalytic amount of piperidine was added. The reaction mixture was refluxed for 6 h with stirring and then cooled to room temperature. The blue solid was filtered and recrystallized from ethanol to give **25a** (7.89 g, 78%). Spectral properties are in agreement with those in the literature:[19,50] mp 242−243 °C; $\lambda_{max}$ ($CHCl_3$) 573 $\log_{10}\varepsilon$ 4.83, (1,4-dioxane) 531 $\log_{10}\varepsilon$ 4.71, (DMF) 587 $\log_{10}\varepsilon$ 4.32, (MeOH) 577 $\log_{10}\varepsilon$ 4.85, (THF) 567 $\log_{10}\varepsilon$ 4.80; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.91 (1 H, d, $J$ = 15.8 Hz, C**H**═CH), 7.75 (2 H, d, $J$ = 9.0 Hz, Ar**H**), 6.86 (1 H, d, $J$ = 15.7 Hz, CH═C**H**), 6.86 (2 H, d, $J$ = 9.2 Hz, Ar**H**), 4.79 (1 H, br s, OH), 3.64−3.56 (4H, m, N(C**H**$_2$)$_2$O) 3.12 (3 H, s, NC**H**$_3$), 1.75 (6 H, s, C(C**H**$_3$)$_2$).

**2-(4-((2-Hydroxyethyl)(methyl)amino)benzylidene)malononitrile (25b).** 4-((2-Hydroxyethyl)(methyl)amino)benzaldehyde **24** (3.6 g, 20 mmol) and malononitrile (1.6 g, 24 mmol) were refluxed in toluene (30 mL) for 3.5 h in the presence of acetic acid (0.3 mL) and ammonium acetate (0.1 g). The solvent was removed in vacuo, and the crude product was recrystallized from ethanol to give **25b** (2.9 g, 63%) as a pale brown solid. Spectral properties are in agreement with the literature:[51,52] mp 98−100 °C; $\lambda_{max}$ ($CHCl_3$) 432 $\log_{10}\varepsilon$ 4.72, (1,4-dioxane) 423 $\log_{10}\varepsilon$ 4.69, (DMF) 441 $\log_{10}\varepsilon$ 4.71, (MeOH) 430 $\log_{10}\varepsilon$ 4.70, (THF) 431 $\log_{10}\varepsilon$ 4.71; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.83 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 7.46 (1 H, s, C**H**═C(CN)$_2$), 6.80 (2 H, d, $J$ = 9.2 Hz, Ar**H**), 3.92 (2 H, t, $J$ = 5.6 Hz, NC**H**$_2$CH$_2$OH), 3.69 (2 H, t, $J$ = 5.6 Hz, NCH$_2$C**H**$_2$OH), 3.21 (3 H, s, C**H**$_3$).

**(*E*)-4-(2-((4-(2-(4-Cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)phenyl)(methyl)amino)ethoxy)-4-oxobutanoic acid (26a).** To a solution of **25a** (1.0 g, 2.6 mmol) and succinic anhydride (0.51 g, 5.1 mmol) in anhydrous dichloromethane (30 mL), 4-dimethylaminopyridine (0.31 g, 2.6 mmol) and pyridine (0.65 mL, 8.0 mmol) were added under $N_2$. The reaction mixture was stirred at room temperature overnight and then washed with brine (30 mL) and water (30 mL). The organic phase was dried over $Na_2SO_4$, and the solvent was concentrated in vacuo. The residue was purified by column chromatography on silica (5% ethanol in DCM) to give **26a** (0.91 g, 77%) as a blue/purple powder. Spectral properties are in agreement with the literature:[19,50] mp 202−203 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.92 (1 H, d, $J$ = 15.9 Hz, C**H**═CH), 7.78 (2 H, d, $J$ = 9.2 Hz, Ar**H**), 6.90 (1 H, d, $J$ = 15.7 Hz, CH═C**H**), 6.88 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 4.25 (2 H, t, $J$ = 5.5 Hz, NCH$_2$C**H**$_2$O), 3.77 (2 H, t, $J$ = 5.4 Hz, NC**H**$_2$CH$_2$O), 3.10 (3 H, s, NC**H**$_3$), 2.51−2.49 (2 H, m, HOOCC**H**$_2$CH$_2$CO), 2.46−2.43 (2 H, m, HOOCCH$_2$C**H**$_2$CO), 1.76 (6 H, s, C(C**H**$_3$)$_2$).


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**4-(2-((4-(2,2-Dicyanovinyl)phenyl)(methyl)amino)ethoxy)-4-oxobutanoic Acid (26b).** To a solution of **25b** (1.5 g, 6.6 mmol) and succinic anhydride (1.32 g, 13.2 mmol) in anhydrous dichloromethane (70 mL), DMAP (0.81 g, 6.6 mmol) and pyridine (1.7 mL, 20 mmol) were added under $N_2$. The reaction mixture was stirred at room temperature overnight and then washed with brine (50 mL) and water (50 mL). The organic phase was dried over $Na_2SO_4$, and the solvent was concentrated in vacuo. The residue was purified by column chromatography on silica (5% ethanol in DCM) to give **26b** (1.51 g, 70%) as a yellow solid. Spectral properties are in agreement with the literature:[53] $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.82 (2 H, d, $J$ = 9.1 Hz, Ar**H**), 7.48 (1 H, s, C**H**=C(CN)$_2$), 6.76 (2 H, d, $J$ = 9.2 Hz, Ar**H**), 4.34 (2 H, t, $J$ = 5.8 Hz, OC**H**$_2$CH$_2$N), 3.76 (2H, t, $J$ = 5.8 Hz, OCH$_2$C**H**$_2$N), 3.15 (1 H, s, NC**H**$_3$), 2.66−2.62 (2 H, m, HOOCC**H**$_2$CH$_2$CO), 2.62−2.59 (2 H, m, HOOCCH$_2$C**H**$_2$CO).

**2-((4-((*E*)-2-(4-Cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)phenyl)(methyl)amino)ethyl 2-((*Z*)-4-((*E*)-3-(4-Cyano-5-(dicyanomethylene)-2,2-dioctyl-2,5-dihydrofuran-3-yl)allylidene)quinolin-1(4*H*)-yl)ethyl Succinate (MC5).** The acid **26a** (729 mg, 1.58 mmol) and the alcohol **23** (938 mg, 1.58 mmol) were dissolved in a mixture of anhydrous DCM (50 mL) and anhydrous DMF (2.5 mL). Dicyclohexylcarbodiimide (DCC) (444 mg, 1.58 mmol) and DMAP (193 mg, 1.58 mmol) were added, and the ensuing mixture was stirred at room temperature for 24 h. The resulting solution was diluted with DCM (50 mL) and washed with brine (100 mL) and water (100 mL). The organic phase was dried over $MgSO_4$, and the solvent was concentrated in vacuo. The residue was purified by column chromatography on silica (0:1 → 3:7 acetone/DCM) to give **MC5** (301 mg, 18%) as a dark blue solid: mp 121−123 °C; $\lambda_{max}$ ($CHCl_3$) 698 $\log_{10}\varepsilon$ 5.23, (1,4-dioxane) 698 $\log_{10}\varepsilon$ 5.16, (DMF) 667 $\log_{10}\varepsilon$ 5.06, (MeOH) 662 $\log_{10}\varepsilon$ 4.98, (THF) 692 $\log_{10}\varepsilon$ 5.15; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ ppm: 8.94 (1 H, br s, CH=C**H**=CH), 8.25 (1 H, d, $J$ = 8.4 Hz, Ar**H** (quinoline)), 7.83 (1 H, dd, $J$ = 7.8, 7.8 Hz, Ar**H** (quinoline)), 7.72 (1 H, br d, $J$ = 5.9 Hz, CH (pyridine ring)), 7.66−7.60 (2 H, m, Ar**H** (quinoline), CC**H**=CHC), 7.59−7.54 (3 H, m, Ar**H**, Ar**H** (quinoline)), 7.24−7.18 (1 H, m, CH (pyridine ring)), 6.78 (2 H, d, $J$ = 8.9 Hz, Ar**H**), 6.73 (1 H, d, $J$ = 15.9 Hz, CCH=C**H**C), 6.71 (1 H, d, $J$ = 13.0 Hz, C**H**=CH=CH), 5.73 (1 H, br s, CH=CH=C**H**), 4.62−4.57 (2 H, m, N(C**H**$_2$)$_2$OC=O), 4.56−4.52 (2 H, m, N(C**H**$_2$)$_2$OC=O), 4.38 (2 H, t, $J$ = 5.3 Hz, CH$_3$N(C**H**$_2$)$_2$O), 3.78 (2 H, t, $J$ = 5.5 Hz, CH$_3$N(C**H**$_2$)$_2$O), 3.15 (1 H, s, NC**H**$_3$), 2.60−2.52 (4 H, m, CC**H**$_2$C**H**$_2$C), 1.97−1.89 (2 H, CH$_2$ (C$_8$ chain)), 1.74 (6 H, s, C(C**H**$_3$)$_2$), 1.71−1.60 (2 H, m, CH$_2$ (C$_8$ chain)), 1.33−1.06 (24 H, m, CH$_2$ (C$_8$ chain)), 0.85 (6 H, t, $J$ = 6.9 Hz, CH$_3$ (C$_8$ chain)); $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 1:1, 8.78 (0.5 H, t, $J$ = 13.3, 13.3 Hz, CH=C**H**=CH), 8.68 (0.5 H, d, $J$ = 8.6 Hz, Ar**H** (quinoline)), 8.64 (0.5 H, d, $J$ = 6.6 Hz, CH (pyridine ring)), 8.58 (0.5 H, d, $J$ = 8.1 Hz, Ar**H** (quinoline)), 8.49 (0.5 H, d, $J$ = 6.6 Hz, CH (pyridine ring)), 8.26 (0.5 H, d, $J$ = 8.5 Hz, Ar**H** (quinoline)), 8.20 (0.5 H, d, $J$ = 8.9 Hz, Ar**H** (quinoline)), 8.08−7.99 (1.5 H, m, 0.5 H CH (pyridine ring), 2 × 0.5 H Ar**H** (quinoline)), 7.96−7.85 (1.5 H, m, 0.5 H CH=C**H**=CH, 1 H CC**H**=CHC), 7.83−7.70 (3 H, m, 2H Ar**H**, 2 × 0.5 H Ar**H** (quinoline)), 7.42 (1 H, d, $J$ = 6.9 Hz, CH (pyridine ring)), 7.30 (0.5 H, d, $J$ = 13.7 Hz, C**H**=CH=CH), 7.20 (0.5 H, d, $J$ = 13.7 Hz, C**H**=CH=CH), 6.90−6.79 (3 H, m, 2H Ar**H**, 1 H CCH=C**H**C), 6.31 (0.5 H, d, $J$ = 12.6 Hz, CH=CH=C**H**), 5.94 (0.5 H, d, $J$ = 12.8 Hz, CH=CH=C**H**), 4.93 (2 H, br s, N(C**H**$_2$)$_2$OC=O), 4.52−4.45 (2 H, m, N(C**H**$_2$)$_2$OC=O), 4.21−4.15 (2 H, m, CH$_3$N(C**H**$_2$)$_2$O), 3.71 (2 H, t, $J$ = 4.6 Hz, CH$_3$N(C**H**$_2$)$_2$O), 3.04 (3 H, s, NC**H**$_3$), 2.45−2.36 (4 H, m, CC**H**$_2$C**H**$_2$C), 2.23−2.13 (1 H, m, CH$_2$ (C$_8$ chain)), 2.07−1.97 (1 H, m, CH$_2$ (C$_8$ chain)), 1.94−1.84 (1 H, m, CH$_2$ (C$_8$ chain)), 1.82−1.65 (1 H, m, CH$_2$ (C$_8$ chain)), 1.76 (6 H, s, C(C**H**$_3$)$_2$), 1.30−1.05 (24 H, m, CH$_2$ (C$_8$ chain)), 0.81 (3 H, t, $J$ = 6.2 Hz, CH$_3$ (C$_8$ chain)), 0.74−0.68 (3 H, m, CH$_3$ (C$_8$ chain)); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 178.9, 176.3, 174.6, 172.2, 172.0, 167.3, 153.1, 150.8, 148.6, 144.3, 141.2, 138.1, 133.4, 132.4, 126.4, 125.7, 124.9, 122.5, 116.9, 116.1, 115.5, 115.0, 112.6, 112.5, 112.0, 111.6, 110.2, 109.2, 109.1, 106.4, 100.0, 97.1, 94.2, 61.9, 61.4, 54.6, 52.8, 50.8, 46.2, 39.3, 39.1, 31.8, 29.5, 29.3, 29.2, 28.7, 26.7, 22.6, 14.1; $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 1:1, 177.8, 177.3, 176.4, 175.5, 171.7, 171.6, 171.5, 162.3, 162.1, 161.2, 152.9, 152.0, 151.7, 149.1, 144.9, 143.8, 141.6, 141.2, 138.1, 138.0, 134.0, 133.7, 132.7, 127.5, 127.2, 125.9, 125.6, 124.9, 122.3, 118.2, 117.9, 117.2, 116.2, 115.7, 115.6, 114.1, 113.7, 113.3, 112.7, 112.5, 112.3, 111.8, 111.5,110.2, 108.8, 107.4, 105.5, 99.1, 98.5, 98.2, 92.7, 80.5, 76.3, 61.9, 61.6, 61.5, 53.5, 52.9, 51.4, 50.0, 39.0, 38.7, 38.6, 31.2, 28.8, 28.7, 28.5, 28.4, 28.4, 28.3, 25.6, 22.0, 13.9, 13.8; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{63}H_{70}N_8O_6Na$: 1057.5316; found: 1057.5311 Δ 0.5 ppm.

**2-((*Z*)-4-((*E*)-3-(4-Cyano-5-(dicyanomethylene)-2,2-dioctyl-2,5-dihydrofuran-3-yl)allylidene)quinolin-1(4*H*)-yl)ethyl 2-((4-(2,2-Dicyanovinyl)phenyl)(methyl)amino)ethyl Succinate (MC6).** The acid **26b** (720 mg, 2.20 mmol) and the alcohol **23** (2.6 g, 4.39 mmol) were dissolved in a mixture of anhydrous DCM (50 mL) and anhydrous DMF (2.5 mL). DCC (545 mg, 2.64 mmol) and DMAP (323 mg, 2.64 mmol) were added, and the ensuing mixture was stirred at room temperature for 24 h. The resulting solution was diluted with DCM (50 mL) and washed with brine (100 mL) and water (100 mL). The organic phase was dried over $MgSO_4$, and the solvent was concentrated in vacuo. The residue was purified by column chromatography on silica (1:9 ethyl acetate:petroleum spirits) to give **MC6** (346 mg, 17%) as a dark green solid: mp 91−93 °C; $\lambda_{max}$ ($CHCl_3$) 698 $\log_{10}\varepsilon$ 5.21, (1,4-dioxane) 698 $\log_{10}\varepsilon$ 5.15, (DMF) 668 $\log_{10}\varepsilon$ 5.05, (MeOH) 662 $\log_{10}\varepsilon$ 5.02, (THF) 692 $\log_{10}\varepsilon$ 5.16; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 1:1, 8.77 (0.5 H, dd, $J$ = 13.0, 13.0 Hz, CH=C**H**=CH), 8.68 (0.5 H, d, $J$ = 8.4 Hz, Ar**H**(quinoline)), 8.65 (0.5 H, d, $J$ = 6.9 Hz, C**H** (pyridine ring)), 8.57 (0.5 H, d, $J$ = 8.6 Hz, Ar**H**(quinoline)), 8.48 (0.5 H, d, $J$ = 6.9 Hz, C**H** (pyridine ring)), 8.25 (0.5 H, d, $J$ = 8.7 Hz, Ar**H**(quinoline)), 8.19 (0.5 H, d, $J$ = 8.6 Hz, Ar**H**(quinoline)), 8.08−7.97 (2.5 H, m, 2 × 0.5 H Ar**H**(quinoline), 1 H C**H**=(CN)$_2$, 0.5 H C**H** (pyridine ring)), 7.93 (0.5 H, dd, $J$ = 13.4, 13.4 Hz, CH=C**H**=CH), 7.85−7.70 (3 H, m, 2 H Ar**H**, 2 × 0.5 H Ar**H**(quinoline)), 7.42 (0.5 H, d, $J$ = 6.9 Hz, C**H** (pyridine ring)), 7.30 (0.5 H, d, $J$ = 13.6 Hz, C**H**=CH=CH), 7.19 (0.5 H, d, $J$ = 13.9 Hz, C**H**=CH=CH), 6.88−6.83 (2 H, m, Ar**H**), 6.30 (0.5 H, d, $J$ = 12.9 Hz, CH=CH=C**H**), 5.93 (0.5 H, d, $J$ = 12.4 Hz, CH=CH=C**H**), 4.95−4.90 (2 H, m, N(C**H**$_2$)$_2$OC=O), 4.51−4.56 (2 H, m, N(C**H**$_2$)$_2$OC=O), 4.16 (2 H, t, $J$ = 5.2 Hz, CH$_3$N(C**H**$_2$)$_2$O), 3.71 (2 H, t, $J$ = 5.3 Hz, CH$_3$N(C**H**$_2$)$_2$O), 3.03 (3 H, s, NC**H**$_3$), 2.46−2.35 (4 H, m, CC**H**$_2$C**H**$_2$C), 2.23−2.12 (1 H, m, CH$_2$ (C$_8$ chain)), 2.06−1.95 (1 H, m, CH$_2$ (C$_8$ chain)), 1.93−1.82 (1 H, m, CH$_2$ (C$_8$ chain)), 1.75−1.65 (1 H, m, CH$_2$ (C$_8$ chain)), 1.27−1.07 (24 H, m, CH$_2$ (C$_8$ chain)), 0.81 (3 H, t, $J$ = 6.5 Hz, CH$_3$ (C$_8$ chain)), 0.71 (3 H, t, $J$ = 6.1 Hz, CH$_3$ (C$_8$ chain)); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ ppm: 8.93 (1 H, br s, CH=C**H**=CH), 8.25 (1 H, d, $J$ = 8.4 Hz, Ar**H**(quinoline)),), 7.82 (1 H, dd, $J$ = 7.6, 7.6 Hz, Ar**H**(quinoline)), 7.77 (2 H, d, $J$ = 8.8 Hz, Ar**H**), 7.71 (1 H, br s, C**H** (pyridine ring)), 7.67−7.60 (1 H, m, Ar**H**(quinoline)),), 7.57 (1 H, dd, $J$ = 7.6, 7.6 Hz, Ar**H**(quinoline)),), 7.42 (1 H, s, C**H**=(CN)$_2$), 7.20 (1 H, br s, C**H** (pyridine ring)), 6.77−6.69 (3 H, m, Ar**H**, C**H**=CH=CH), 5.73 (1 H, br s, CH=CH=C**H**), 4.59 (2 H, br s, N(C**H**$_2$)$_2$OC=O), 4.53 (2 H, t, $J$ = 4.5 Hz, N(C**H**$_2$)$_2$OC=O), 4.39−4.34 (2 H, m, CH$_3$N(C**H**$_2$)$_2$O), 3.75 (2 H, t, $J$ = 5.4 Hz, CH$_3$N(C**H**$_2$)$_2$O), 3.14 (3 H, s, NC**H**$_3$), 2.58−2.50 (4 H, m, CC**H**$_2$C**H**$_2$C), 1.7−1.88 (2 H, m, CH$_2$ (C$_8$ chain)), 1.73−1.56 (2 H, m, CH$_2$ (C$_8$ chain)), 1.31−1.05 (24 H, m, CH$_2$ (C$_8$ chain)), 0.84 (3 H, t, $J$ = 6.8 Hz, CH$_3$ (C$_8$ chain)); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 178.9, 172.1, 171.9, 167.2, 158.0, 153.6, 150.7, 144.2, 141.1, 138.0, 133.8, 133.3, 126.4, 125.6, 124.8, 119.7, 116.0, 115.7, 115.4, 114.9, 114.7, 111.9, 110.1, 109.1, 106.5, 99.9, 72.4, 61.7, 61.4, 52.7, 50.7, 49.1, 39.3, 38.9, 31.7, 29.5, 29.3, 29.2, 28.6, 25.6, 24.9 22.5, 14.0; HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{55}H_{63}N_7O_5Na$: 924.4788; found: 924.4796 Δ = 0.9 ppm.

**6,6′-(Phenylazanediyl)dihexan-1-ol (28).** A mixture of freshly distilled aniline (4.6 mL, 50 mmol), 6-chloro-1-hexanol **27** (14.7 mL, 110 mmol), and potassium carbonate (15.2 g, 110 mmol) were heated in freshly distilled *n*-butanol (25 mL) under reflux for 4 days. The solution was cooled to room temperature, and the solids were removed by filtration. The filtrate was then concentrated in vacuo, and


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the residue was purified by column chromatography on silica (2:3 ethyl acetate: petroleum ether) to give **28** (5.9 g, 41%) as a colorless oil. Spectral properties are in agreement with the literature:[54−57] $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.20 (2H, dd, $J$ = 8.6, 7.3 Hz, Ar**H**), 6.66−6.61 (3H, m, Ar**H**), 3.64 (4H, t, $J$ = 6.6 Hz, C$\mathbf{H}_2$OH), 3.26 (4H, t, $J$ = 7.6 Hz, NC$\mathbf{H}_2$), 1.64−1.55 (4H, m, C$\mathbf{H}_2$), 1.44−1.32 (8H, m, C$\mathbf{H}_2$).

**6,6′-(4-Formylphenylazanediyl)bis(hexane-6,1-diyl) Diacetate (29).** To a solution of **28** (4.5 g, 15.3 mmol) in acetic anhydride (5 mL), pyridine (3.7 mL, 45.6 mmol) was added. The reaction mixture was refluxed for 16 h with stirring and then cooled to room temperature. The solution was then poured into iced water (100 mL) and extracted with DCM (3 × 100 mL). The combined organic phases were then washed with brine (3 × 300 mL), dried over $MgSO_4$, and concentrated in vacuo to give the diacetyl-protected derivative of **28** ((phenylazanediyl)bis(hexane-6,1-diyl) diacetate) as a pale yellow oil (5.78 g, quant. yield). The crude product was found to be suitable for use without further purification.

Phosphorus oxychloride (1.7 mL, 18.4 mmol) was added dropwise to anhydrous DMF (10 mL) at 0 °C. After stirring the mixture for 30 min at 0 °C, the diacetyl-protected derivative of **28** ((phenylazanediyl)bis(hexane-6,1-diyl) diacetate) (5.78g, 15.3 mmol) in DMF (min amount) was added via a dropping funnel, and the resulting solution was heated at 90 °C for 2 h. The reaction mixture was then cooled to room temperature and poured over ice (80 g). The solution was then neutralized to pH 6−8 by dropwise addition of sat. sodium acetate solution. The mixture was twice extracted with DCM (80 mL), and the combined organic layers were washed with water (150 mL), dried over $MgSO_4$, and concentrated in vacuo to give **29** as a pale yellow oil (4.34 g, 70%). The product was found to be suitable for use without further purification. Spectral properties are in agreement with the literature:[54] $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 9.68 (1 H, s, C**H**O), 7.68 (2 H, d, $J$ = 9.0 Hz, Ar**H**), 6.61 (2 H, d, $J$ = 9.0 Hz, Ar**H**), 4.04 (4 H, t, $J$ = 6.7 Hz, C$\mathbf{H}_2$O), 3.34−3.30 (4 H, m, NC$\mathbf{H}_2$), 2.02 (6 H, s, C$\mathbf{H}_3$), 1.66−1.56 (8 H, m, C$\mathbf{H}_2$), 1.43−1.30(8 H, m, C$\mathbf{H}_2$).

**4,4′-(6,6′-(4-Formylphenylazanediyl)bis(hexane-6,1-diyl)bis-(oxy))bis(4-oxobutanoic Acid) (30).** Compound **29** (4.00 g, 10.7 mmol) was dissolved in methanol (30 mL) and aq $Na_2CO_3$ (25% w/v, 10 mL). The solution was then refluxed for 16 h. The solution was allowed to cool to rt and neutralized with aq. HCl. It was then extracted with DCM (3 × 50 mL), and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the free alcohol 4-(bis(6-hydroxyhexyl)amino)benzaldehyde as a pale yellow oil (2.04 g, 59%): $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 9.69 (1 H, s, C**H**O), 7.69 (2 H, d, $J$ = 8.9 Hz, Ar**H**), 6.64 (2 H, d, $J$ = 8.8 Hz, Ar**H**), 3.65 (4 H, t, $J$ = 6.5 Hz, C$\mathbf{H}_2$OH), 3.36−3.33 (4 H, m, NC$\mathbf{H}_2$), 1.67−1.56 (8 H, m, C$\mathbf{H}_2$), 1.46−1.34 (8 H, m,C$\mathbf{H}_2$); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 190.0, 152.4, 132.2, 124.9, 111.0, 62.7, 51.1, 32.6, 27.1, 26.8, 25.6. HRMS (ESI): $m/z$ $[M + H]^+$ calcd for $C_{19}H_{32}NO_3$: 322.2382; found: 322.2375 Δ = 2.2 ppm.

To a solution of 4-(bis(6-hydroxyhexyl)amino)benzaldehyde (0.80 g, 2.49 mmol) and succinic anhydride (0.99 g, 9.91 mmol) in anhydrous dichloromethane (60 mL), DMAP (0.60 g, 4.94 mmol) and pyridine (1.3 mL, 15.8 mmol) were added under $N_2$. The reaction mixture was stirred at room temperature overnight and then washed with 1 M aq. HCl (50 mL), brine (50 mL), and water (50 mL). The organic phase was dried over $Na_2SO_4$, and the solvent was concentrated in vacuo to give **30** (1.27 g, 97%) as a colorless oil. The product was found to be suitable for use without further purification: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 9.69 (1 H, s, C**H**O), 7.71 (2 H, d, $J$ = 8.8 Hz, Ar**H**), 6.67 (2 H, br d, $J$ = 6.1 Hz, Ar**H**), 4.12 (4 H, t, $J$ = 6.4 Hz, C$\mathbf{H}_2$O), 3.31−3.27 (4 H, m, NC$\mathbf{H}_2$), 2.62−2.59 (4 H, m, C(O)C$\mathbf{H}_2$CH$_2$C(O)), 2.55−2.52 (4 H, m, C(O)CH$_2$C$\mathbf{H}_2$C(O)), 1.62−1.53 (8 H, m, C$\mathbf{H}_2$($C_6$ chain)), 1.46−1.34 (8 H, m, C$\mathbf{H}_2$($C_6$ chain)); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 190.3, 177.5, 172.3, 152.7, 132.4, 124.5, 110.8, 64.7, 51.0, 29.0, 29.0, 28.5, 27.0, 26.6, 25.7; HRMS (ESI): $m/z$ $[M + H]^+$ calcd for $C_{27}H_{40}NO_9$: 522.2703; found: 522.2695 Δ = 1.5 ppm.

**Bis(2-((*E*)-4-((*E*)-3-(4-cyano-5-(dicyanomethylene)-2,2-dioctyl-2,5-dihydrofuran-3-yl)allylidene)quinolin-1(4*H*)-yl)ethyl) 6,6′-Bis(4-formylphenylazanediyl)bis(hexane-6,1-diyl) Disuccinate (31).** The acid **30** (720 mg, 2.20 mmol) and the alcohol **23** (2.6 g, 4.39 mmol) were dissolved in a mixture of anhydrous DCM (50 mL) and anhydrous DMF (2.5 mL). DCC (545 mg, 2.64 mmol) and DMAP (323 mg, 2.64 mmol) were added, and the ensuing mixture was stirred at room temperature for 24 h. The resulting solution was diluted with DCM (50 mL) and washed with brine (100 mL) and water (100 mL). The organic phase was dried over $MgSO_4$, and the solvent was concentrated in vacuo. The residue was purified by column chromatography on silica (1:9 ethyl acetate:petroleum spirits) to give **31** (346 mg, 17%) as a dark blue oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 9.65 (1 H, s, C**H**O), 8.90 (2 H, br s, CH═C**H**═CH), 8.25 (2 H, d, $J$ = 8.4 Hz, Ar**H**(quinoline ring)), 7.84−7.74 (4 H, m, Ar**H**(quinoline ring), CH(pyridine ring)), 7.71 (2 H, d, $J$ = 8.6 Hz, Ar**H**(quinoline ring)), 7.66 (2 H, d, $J$ = 8.9 Hz, Ar**H**), 7.56 (2 H, t, $J$ = 7.7 Hz, CH(pyridine ring)), 7.27 (2 H, br s, CH(pyridine ring)), 6.72 (2 H, d, $J$ = 13.3 Hz, C**H**═CH═CH), 6.62 (2 H, d, $J$ = 9.0 Hz, Ar**H**), 5.69 (1 H, br s, CH═CH═C**H**), 4.65 (4 H, br s, NCH$_2$CH$_2$O), 4.54 (4 H, t, $J$ = 5.0 Hz, NCH$_2$CH$_2$O), 4.07 (4 H, t, $J$ = 6.6 Hz, (CH$_2$)$_5$C$\mathbf{H}_2$O), 3.30−3.26 (4 H, m, NC$\mathbf{H}_2$(CH$_2$)$_5$), 2.55−2.48 (8 H, m, C(═O)C$\mathbf{H}_2$C$\mathbf{H}_2$C(═O)), 1.97−1.86 (4 H, m, CH$_2$ ($C_8$ chain)), 1.61−1.51 (12 H, m, 8 H CH$_2$ ($C_6$ chain), 4 H CH$_2$ ($C_8$ chain)), 1.35−1.27 (8 H, m, CH$_2$ ($C_6$ chain)), 1.23−1.02 (48 H, m, CH$_2$ ($C_8$ chain)), 0.83 (12 H, t, $J$ = 6.9 Hz, CH$_3$ ($C_8$ chain)); $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 1:1, 9.60 (1 H, s, C**H**O), 8.77 (1 H, t, $J$ = 13.0 Hz, CH═C**H**═CH), 8.69−8.64 (2 H, m, Ar**H**(quinoline ring), C**H**(pyridine ring)), 8.56 (1 H, d, $J$ = 8.2 Hz, Ar**H**(quinoline ring)), 8.48 (1 H, d, $J$ = 6.9 Hz, C**H**(pyridine ring)), 8.26 (1 H, d, $J$ = 8.6 Hz, Ar**H**(quinoline ring)), 8.20 (1 H, d, $J$ = 8.5 Hz, Ar**H**(quinoline ring)), 8.07−7.97 (3 H, m, 2H Ar**H**(quinoline ring), 1H CH(pyridine ring)), 7.93 (1 H, t, $J$ = 12.9 Hz, CH═C**H**═CH), 7.81−7.76 (1 H, m, Ar**H**(quinoline ring)), 7.75−7.71 (1 H, m, Ar**H**(quinoline ring)), 7.62 (2 H, d, $J$ = 8.4 Hz, Ar**H**), 7.40 (1 H, d, $J$ = 6.9 Hz, C**H**(pyridine ring)), 7.28 (1 H, d, $J$ = 13.9 Hz, C**H**═CH═CH), 7.18 (1 H, d, $J$ = 13.8 Hz, C**H**═CH═CH), 6.69 (2 H, d, $J$ = 8.8 Hz, Ar**H**), 6.30 (1 H, d, $J$ = 12.8 Hz, CH═CH═C**H**), 5.91 (1 H, d, $J$ = 12.5 Hz, CH═CH═C**H**), 4.96−4.91 (4 H, m, NCH$_2$CH$_2$O), 4.51−4.45 (4 H, m, NCH$_2$CH$_2$O), 3.92−3.85 (4 H, m, (CH$_2$)$_5$C$\mathbf{H}_2$O), 3.34−3.27 (4 H, m, NC$\mathbf{H}_2$(CH$_2$)$_5$), 2.47−2.40 (8 H, m, C(═O)C$\mathbf{H}_2$C$\mathbf{H}_2$C(═O)), 2.23−2.12 (2 H, m, CH$_2$ ($C_8$ chain)), 2.05−1.96 (1 H, m, CH$_2$ ($C_8$ chain)), 1.91−1.85 (1 H, m, CH$_2$ ($C_8$ chain)), 1.73−1.64 (1 H, m, CH$_2$ ($C_8$ chain)), 1.54−1.42 (8 H, m, CH$_2$ ($C_6$ chain)), 1.36−1.03 (56 H, m, 8H CH$_2$ ($C_6$ chain), 48H CH$_2$ ($C_8$ chain)), 0.79 (6 H, t, $J$ = 6.5 Hz, CH$_3$ ($C_8$ chain)), 0.71 (6 H, t, $J$ = 6.1 Hz, CH$_3$ ($C_8$ chain)); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 189.9, 178.9, 172.3, 172.1, 166.7, 152.6, 151.0, 144.2, 141.4, 138.2, 133.4, 132.2, 126.5, 125.5, 124.9, 124.6, 116.3, 115.5, 115.2, 110.8, 110.4, 109.6, 106.3, 99.9, 81.4, 64.9, 61.4, 53.8, 52.9, 50.9, 39.4, 31.8, 29.5, 29.3, 29.2, 28.8, 28.5, 27.1, 26.6, 25.7, 22.6, 14.1; HRMS (ESI): $m/z$ $[M + Na]^+$ calcd for $C_{103}H_{131}N_9O_{11}Na$: 1692.9866; found: 1692.9878 Δ = 0.7 ppm.

**6,6′-Bis(4-((*E*)-2-(4-cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)phenylazanediyl)bis(hexane-6,1-diyl) Bis(2-((*E*)-4-((*E*)-3-(4-cyano-5-(dicyanomethylene)-2,2-dioctyl-2,5-dihydrofuran-3-yl)allylidene)quinolin-1(4*H*)-yl)ethyl) Disuccinate (MC7).** To a solution of **31** (850 mg, 0.51 mmol) and 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile (152 mg, 0.76 mmol) in acetic anhydride (20 mL), a catalytic amount of piperidine was added. The reaction mixture was refluxed for 6 h with stirring and then cooled to room temperature. The solution was concentrated in vacuo to give a blue oil, which was purified by column chromatography on silica (3:7 ethyl acetate/DCM) to give **MC7** (150 mg, 16%) as a dark blue solid: mp 110−112 °C; $\lambda_{max}$ ($CHCl_3$) 697 $\log_{10}\varepsilon$ 5.10, (1,4-dioxane) 635 $\log_{10}\varepsilon$ 4.96 (ZWI 694 $\log_{10}\varepsilon$ 4.93), (DMF) 666 $\log_{10}\varepsilon$ 5.13, (MeOH) 653 $\log_{10}\varepsilon$ 4.75, (THF) 692 $\log_{10}\varepsilon$ 5.18; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.92 (2 H, br s, CH═C**H**═CH), 8.26 (2 H, d, $J$ = 8.2 Hz, Ar**H**(quinoline ring)), 7.91−7.81 (4 H, m, 2H CH(pyridine ring), 2H Ar**H**(quinoline ring)), 7.71 (2 H, d, $J$ = 8.8 Hz, Ar**H**(quinoline ring)), 7.66 (1 H, d, $J$ = 15.6 Hz, C**H**═CH), 7.61−7.56 (2 H, m, Ar**H**(quinoline ring)), 7.54 (2 H, d, $J$ = 8.9 Hz,


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ArH), 7.26 (1 H, br s, CH(pyridine ring)), 6.77−6.64 (5 H, m, 2H CH=CH=CH, 2H ArH, 1H CH=CH), 5.70 (2 H, br s, CH=CH=CH), 4.68−4.59 (4 H, m, $CH_2$ ($NCH_2CH_2O$)), 4.55 (4 H, t, $J$ = 4.8 Hz, $CH_2$ ($NCH_2CH_2O$)), 4.08 (4 H, t, $J$ = 6.5 Hz, $CH_2$), 3.44−3.36 (4 H, m, $CH_2$), 2.66−2.53 (8 H, m, C(=O)$CH_2CH_2$C(=O)), 1.97−1.85 (4 H, m, $CH_2$), 1.73 (6 H, s, $C(CH_3)_2$), 1.69−1.58 (12 H, m, $CH_2$), 1.44−1.35 (8 H, m, $CH_2$), 1.30−1.08 (48 H, m, $CH_2$), 0.83 (12 H, t, $J$ = 6.8 Hz, $CH_3$ ($C_8$ chain)); $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: Two rotamers approximately 1:1, 8.76 (1 H, t, $J$ = 12.9 Hz, CH=CH=CH), 8.69−8.62 (2 H, m, ArH(quinoline ring), CH(pyridine ring)), 8.56 (1 H, d, $J$ = 8.1 Hz, ArH(quinoline ring)), 8.47 (1 H, d, $J$ = 6.6 Hz, CH(pyridine ring)), 8.25 (1 H, d, $J$ = 8.7 Hz, ArH(quinoline ring)), 8.20 (1 H, d, $J$ = 8.6 Hz, ArH(quinoline ring)), 8.07−7.84 (5 H, m, 2H ArH(quinoline ring), 1H CH(pyridine ring), 1H CH=CH, 1H CH=CH=CH), 7.78 (1 H, t, $J$ = 7.2 Hz, ArH(quinoline ring)), 7.75−7.68 (3 H, m, 1H ArH(quinoline ring), 2H ArH), 7.39 (1 H, d, $J$ = 6.5 Hz, CH(pyridine ring)), 7.28 (1 H, d, $J$ = 13.2 Hz, CH=CH=CH), 7.18 (1 H, d, $J$ = 13.3 Hz, CH=CH=CH), 6.86−6.73 (3 H, m, 1H CH=CH, 2H ArH), 6.29 (1 H, d, $J$ = 12.8 Hz, CH=CH=CH), 5.91 (1 H, d, $J$ = 12.4 Hz, CH=CH=CH), 4.93 (4 H, br s, $NCH_2CH_2O$), 4.51−4.45 (4 H, m, $NCH_2CH_2O$), 3.92−3.83 (4 H, m, $CH_2$), 3.43−3.24 (4 H, m, $CH_2$), 2.47−2.40 (8 H, m, C(=O)$CH_2CH_2$C(=O)), 2.21−2.11 (2 H, m, $CH_2$ ($C_8$ chain)), 2.05−1.94 (1 H, m, $CH_2$ ($C_8$ chain)), 1.90−1.81 (1 H, m, $CH_2$), 1.74 (6 H, s, $C(CH_3)_2$), 1.72−1.64 (1 H, m, $CH_2$), 1.59−1.39 (8 H, m, $CH_2$), 1.37−1.02 (56 H, m, $CH_2$), 0.79 (6 H, t, $J$ = 6.2 Hz, $CH_3$ ($C_8$ chain)), 0.73−0.68 (6 H, m, $CH_3$ ($C_8$ chain)); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 178.9, 176.6, 174.5, 172.3, 172.0, 166.4, 152.5, 151.1, 148.8, 144.2, 141.6, 138.2, 133.5, 132.8, 126.5, 125.6, 125.0, 121.6, 116.9, 116.4, 115.7, 115.3, 112.9, 112.3, 111.9, 110.5, 109.6, 108.1, 106.3, 99.8, 96.9, 92.8, 81.0, 64.9, 64.6, 62.3, 61.4, 53.5, 53.0, 51.1, 39.3, 31.8, 29.5, 29.3, 29.2, 28.8, 28.5, 27.3, 26.7, 26.5, 25.7, 22.6, 14.1; HRMS (ESI): $m/z$ $[M + Na]^+$ calcd for $C_{114}H_{138}N_{12}O_{11}Na$: 1874.0505; found: 1874.0496 $\Delta$ = 0.5 ppm.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures giving $^1$H and $^{13}$C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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