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D-π-A-A-π-D Prototype 2,2′-Bipyridine Dyads Exhibiting Large Structure and Environment-Sensitive Fluorescence: Synthesis, Photophysics, and Computation

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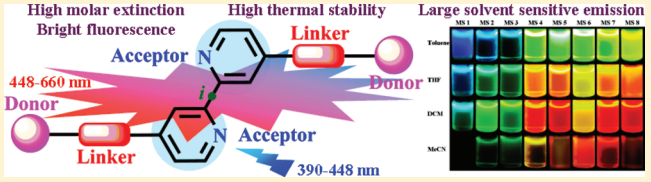
Supporting Information

ABSTRACT: A series of 4,4′-π-conjugated-2,2′-bipyridine chromophores (**MS 1**−**8**) were synthesized, and their photophysical and thermal properties were investigated. The title "push−pull' chromophores", except **MS 1**, were integrated with both alkoxy and alkylamino donor functionalities that differ in their donation capabilities. The oligophenylenevinylene (OPV) chromophores **MS 4**−**8** are associated with a π-extended backbone in which the position and the number of alkoxy donors were systematically varied. All of the studied systems possess a D-π-A-A-π-D dyad archetype in which the A-A is the central 2,2′-bipyridine acceptor core that is electronically attached with the donor termini through π-linkers. The fluorescence quantum yields of the synthesized chromophores are found to be sensitive to the molecular archetype and the solvent medium. Out of the eight fluorescent compounds reported in this article, the compound **MS 5** exhibits fluorescence in the solid state also. The modulating effect of the nature, position, and number of donor functionalities on the optical properties of these classes of compounds has further been comprehended on the basis of DFT and TD-DFT computation in a solvent reaction field.



INTRODUCTION

The phenomenon of fluorescence has turned out to be an indispensable analytical technique in the various branches of science, most prominently, in the fields of analytical, biological, medical sciences, etc.[1] Among the diverse classes of organic π-systems, the materials that absorb electromagnetic radiation by virtue of an intramolecular charge transfer (ICT) and emit from the corresponding photoexcited state are most fascinating because of their notable applications in the field of molecular electronics, integrated photonic devices, non-linear optics (NLO),[2] etc. The elegant fabrication of an electron donor−acceptor (DA) or "push−pull" architecture can be carried out via the electronic union between the donor and acceptor mesomeric units in a chromophore, which is in turn associated with spontaneous charge redistribution between the functionalities (ICT). Consequently, much research has been conducted in designing and synthesizing diverse classes of DA-type fluorescent probes, which are associated with brilliant photophysical behaviors, some typical examples of such fluorescent probes being acridine,[3] fluorescein,[4] cyanine,[5] rhodamine,[6] coumarin,[7] BODIPY,[8] squarines,[9] oligophenylenevinylenes (OPVs),[10] etc.

The disconnection approach is a beautiful tool for organic chemists to devise a wide variety of chromophores wherein the nitrogen-containing heterocycles act as very promising building blocks to synthesize diverse classes of strongly emissive materials.[11] 2,2′-Bipyridine derivatives are endowed with an extensive coordination/supramolecular chemistry.[12] However, in photoscience, it is advantageous to employ this *N*-heterobiaryl compound because of the fact that easy derivatization of the pyridine rings offers introduction of an assorted class of donor end-capping functionalities to tune the optical properties of the relevant 2,2′-bipyridine based dyads. Over the past two decades, many research groups including Le Bozec, Beer, Abbotto, and others have accounted for the diverse end-capped 2,2′-bipyridine chromophores with moderate to strong emission responses.[13−15] Recently, Ajayaghosh and co-workers have exemplified the chemo-sensing properties of the 2,2′-bipyridine based luminophores.[16] Transition metal complexes of the 2,2′-bipyridine based DA systems are of topical interest due to their potential applicability in octupolar nonlinearity.[17] Heteroleptic bis-thiocyanato ruthenium complexes, bearing a TiO_2 anchoring 2,2′-bipyridine ligand along with another auxiliary 2,2′-bipyridine ligand (known as antenna), have proved to be very promising photosensitizers for building high-performance dye-sensitized solar cell modules.[18]

The exciting photophysical responses of the 2,2′-bipyridine based DA systems and their transition-metal complexes have drawn our recent attention.[19] The bipyridine based chromophores reported so far are either symmetrically (point group = C_i) or dissymmetrically (point group = C_1) substituted with alike donor functionalities (for example, alkylamino, etc.), whereas the photophysical properties of the associated heterodonor systems are less explored. In this article, we wish to report a series of styryl- and bistyryl-2,2′-bipyridine luminophores (**MS 2**−**8**, Chart 1) functionalized with both the alkoxy and amino functionalities in C_i symmetrical fashion and their photophysical

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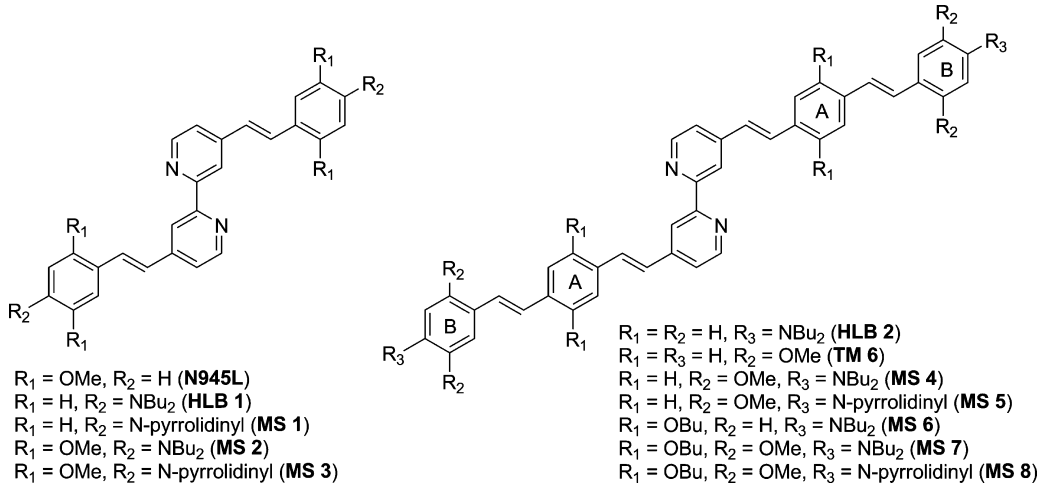
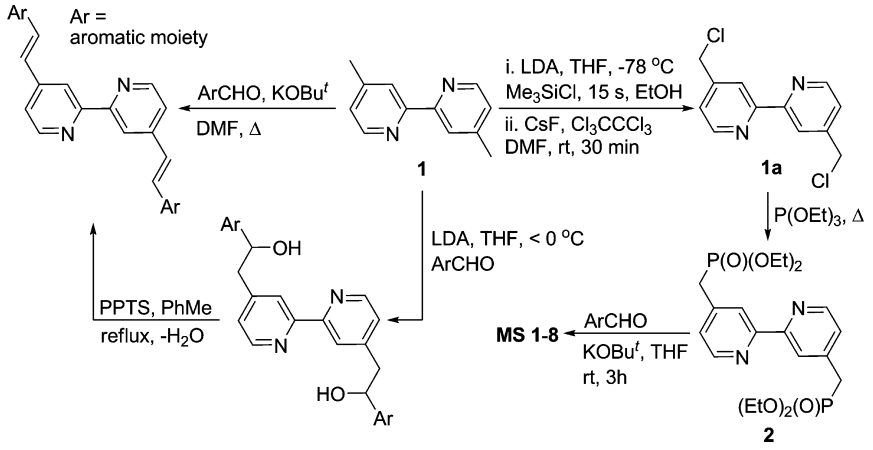
Chart 1. Molecular Structure of the Synthesized and the Parent π-Conjugated-2,2′-bipyridine Chromophores (MS 1−8)[a]



[a]The two phenyl rings of the OPV chromophores were named as A and B for easy discussion in the text.

Scheme 1. Convenient Synthetic Protocols To Access the Symmetrical Bipyridine Chromophores



properties. The prototype of the synthesized dyads is D-π-A-A-π-D (D = donor, A = acceptor) in which the bipyridine moiety acts as the central acceptor core to join the terminal donor functionalities through vinylene linkers. The Horner−Wordsworth−Emmons reaction (HWE) was exclusively used so as to introduce electron-donating groups into the bipyridine central acceptor core unit. The photophysical properties of the synthesized chromophores (**MS 1−8**, Chart 1) were compared with four reported dyes, namely, (a) the blue OLED dye 4,4′-bis(2,5-dimethoxystyryl)-2,2′-bipyridine (known as **N945L**) reported by Nazeeruddin and Grätzel;[15a] (b) 4,4′-bis(4-dibutylaminostyryl)-2,2′-bipyridine (named as **HLB 1** in this article)[13d] and 4,4′-bis(4-(4-dibutylaminostyryl)styryl)-2,2′-bipyridine (named as **HLB 2** in this article)[13h] reported by Le Bozec; and (c) 4,4′-bis(4-(2,5-dimethoxystyryl)styryl)-2,2′-bipyridine (named as **TM 6**) reported by us[19a] (see Chart 1). A pragmatic observation points out that the introduction of the amino donor functionalities to **N945L**/**TM 6** or alkoxy donors to **HLB 1**/**HLB 2** have induced a significant alteration of the photonic responses in the present chromophores. In addition, the position of the alkoxy functionalities attached to the conjugated backbone of the OPV derivatives, **MS 4−8**, greatly influences their photophysical properties. Furthermore, a thorough computational analysis at the level of density functional theory (DFT) in a solvent reaction field was performed to scrutinize the effect of donor positions on the geometrical and electronic parameters of the reference and the synthesized chromophores. All of the synthesized π-conjugated molecules **MS 1−8** fluoresce at room temperature with large Stokes shift, while the emissive behavior of the OPV chromophores **MS 4−8** epitomizes a large sensitivity to the solvent polarity. Among eight fluorescent compounds reported in this article, the compound, **MS 5** is emissive in the solid state also.

RESULTS AND DISCUSSION

Synthesis and Characterization. The bench-top syntheses of the 4,4′-π-conjugated-2,2′-bipyridine chromophores were accomplished via highly efficient synthetic protocol (see Scheme 1). The symmetrically substituted 2,2′-bipyridine derivatives (point symmetry = C_i) can be easily derived either through (a) a Knoevenagel-type reaction between the doubly deprotonated 4,4′-dimethyl-2,2′-bipyridine (**1**) and suitable aromatic aldehydes or (b) a Horner−Wordsworth−Emmons (HWE) reaction between the bis-phosphonate (**2**) and aromatic aldehydes. The Knoevenagel-type reaction triggers at the acidity of the 4-picolyl protons of the bipyridine starting precursor (**1**). A two-step synthetic approach that has been developed entails the deprotonation of **1** by a strong base, e.g., lithium diisopropylamide (LDA)

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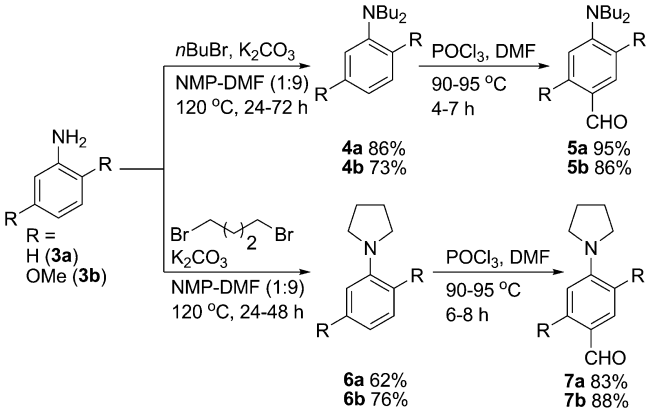
at low temperature followed by nucleophilic addition of the resulting carbanion to an aromatic aldehyde to form a secondary alcohol. The resulting alcohol is then dehydrated, usually by pyridinium *p*-toluene sulfonate (PPTS), to convert it to the corresponding alkene (Scheme 1).[14a] An alternative one-step protocol directly yields the desired alkenes when a mixture of **1** and an aromatic aldehyde is heated in presence of a strong and hindered base, e.g., KOBu^t, in DMF.[13d]

The donor end-capping functionalities in the present bipyridine chromophores (**MS 1−8**) were introduced by the HWE protocol due to its better performance (high yield, *E*-selectivity, etc.) in comparison with the two other methodologies as described in Scheme 1. Also, the conventional Wittig pathway was avoided because of the undesired trouble with the coproduct, triphenylphosphine oxide, during workup and purification. The key intermediate of the HWE pathway is the phosphonate **2**, which has been extensively used in literature to synthesize a diverse class of symmetrically substituted 2,2′-bipyridine chromophores. The concerned intermediate (**2**) is easily derived from the corresponding halomethyl derivatives through an Arbuzov reaction. An initial attempt to brominate **1** through a radical mechanized reaction route (NBS/benzoylperoxide or AIBN) was unsatisfactory for obtaining 4,4′-bis-bromomethyl-2,2′-bipyridine. However, the corresponding chloromethyl derivative, **1a**, was used throughout the present work and was synthesized following an efficient synthetic protocol developed by Fraser and co-workers. The concerned two-step approach involves deprotonation of **1** with LDA and trapping of the resulting carbanion with chlorotrimethylsilane, followed by subsequent chlorination with hexachloroethane in presence of a dry fluoride source, cesium fluoride (CsF).[20] The aldehydes used in the present study are not commercially accessible and thus were synthesized as described in the following sections.

The anilines (**3a−b**) were alkylated in presence of the suitable electrophiles in a *N*-methylpyrrolidinone (NMP)−DMF solvent system to obtain the desired *N*,*N*-dialkyl anilines (**4a−b**, **6a−b**) in good yield (Scheme 2). Subsequently, the

Scheme 2. Synthesis of the Alkylamino Benzaldehydes



Vilsmeier−Haack formylation of the *N*,*N*-dialkyl anilines (**4a−b**, **6a−b**) converts them to the corresponding benzaldehydes (**5a−b**, **7a−b**) with excellent *para*-selectivity.

The π-conjugated benzaldehydes bearing different substitutions were obtained through a two-step synthetic approach as depicted in Table 1. The introduction of different donor functionalities in the corresponding aldehydes (**10b−15b**) was executed via the appropriate selection of the starting materials. The usage of an alkoxy derivatized phosphonate precursor (**9**) allows the introduction of the alkoxy functionalities in the formylated phenyl rings. At the outset, the HWE reaction between the appropriate phosphonate (**8−9**) and the alkylaminobenzaldehydes (**5a−b**, **7a−b**) affords the corresponding bromostilbenes (**10a−15a**) in excellent yield with *E*-selectivity of the C=C bonds. Subsequent lithium−halogen exchange reaction followed by electrophilic quenching with dimethylformamide converts the bromostilbenes (**10a−15a**) to the corresponding benzaldehydes (**10b−15b**) in moderate to good yields (Table 1).

The molecular structures of all of the synthesized bipyridine chromophores (**MS 1−8**) were unambiguously determined through NMR (^{1}H and ^{13}C) and mass (LC−MS and MALDI−TOF/TOF) spectroscopy. The presence of only one set of ^{1}H and ^{13}C signals in the NMR spectra evidently demonstrates the symmetrical structure of the chromophores. The ^{1}H NMR resonances of the pyridine rings and that of the vinylic protons for the chromophores **MS 1−8** are summarized in Table 2. All of the vinylic C=C bonds are found to be in *E*-geometry as indicated by the splitting of each of the CH resonances by the neighboring protons with a $^3J_{HH}$ coupling constant of ca. 16 Hz. However, no trace of the *Z*-isomer was signified in the relevant ^{1}H NMR spectra. A comparison between the ^{1}H NMR signals due to the aromatic protons of the open chain amino donor end-capped chromophore **MS 2** (dibutylamino donor) and its cyclic analogue, i.e., **MS 3** (pyrrolidine donor) reveals that the protons attached *ortho* to the amino functionalities have a larger chemical shift in the case of **MS 2** in comparison with **MS 3** (see Supporting Information). The same trend is observed for the other open chain/cyclic amino donor pairs, viz., **MS 4**/**MS 5** and **MS 7**/**MS 8**. This finding is indicative of a greater donation capability of the cyclic pyrrolidine compared with the corresponding open chain amino donor, dibutylamine.

One Photon Absorption and Emission Properties: (a) Nature of Substituents. The steady-state one photon absorption and emission properties of the synthesized chromophores **MS 1−8** were investigated in four different solvents (see Table 3 and Figure 1). As shown in Figure 1, broad structureless bands of the absorption and emission spectra in the visible region are the chief characteristic features of all of the chromophores in the present study. The molar extinction coefficient (ε) of the lowest energy absorption band of all of the chromophores is fairly high (see Table 3). The low solubility of **MS 1** has precluded measurement of the molar absorptivity with a better accuracy. The origination of the lowest energy band in the absorption spectra of **MS 1−8**, however, is due to an intramolecular $\pi \rightarrow \pi^*$ ICT from the donor-based molecular orbitals to the acceptor (pyridine)-based molecular orbitals in the relevant dipolar chromophores, which in fact was firmly affirmed owing to the sensitivity of the relevant absorption band on the solvent polarity (see Table 3). In addition, the ICT band maxima were found to undergo a bathochromic shift by ca. 15 nm for the pyrrolidine end-capped (cyclic amino donor) chromophores as compared to those of the dibutylamino (open chain amino donor) analogues, viz., **MS 2**/**MS 3**, **MS 4**/**MS 5**, and **MS 7**/**MS 8** in the same solvent medium (Table 3). The rationale for this observation might be due to the greater donation capability of the cyclic pyrrolidine donor compared to the open chain dibutylamino donor (vide supra).

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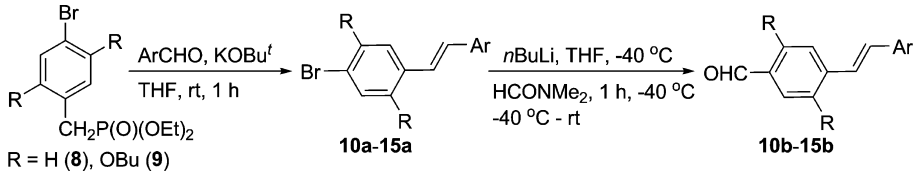
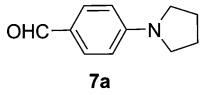
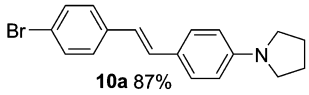
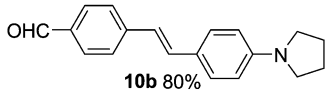
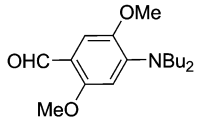
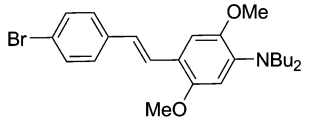
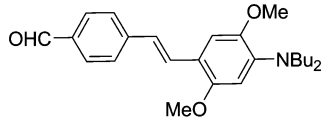
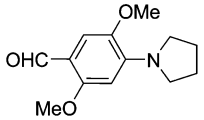
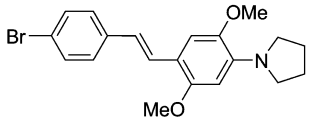
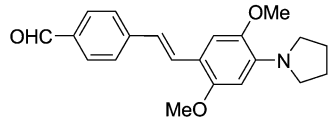
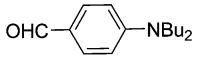
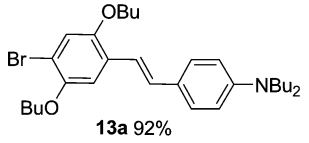
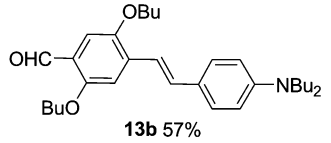
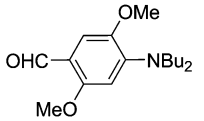
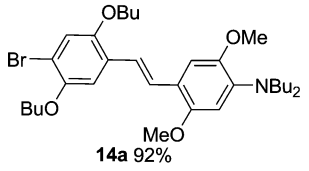
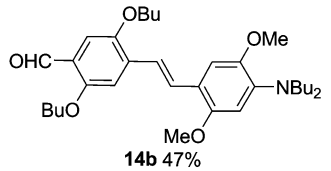
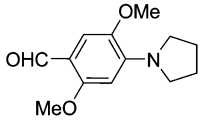
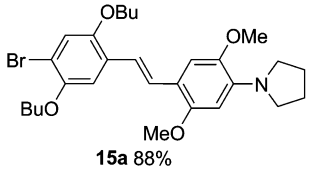
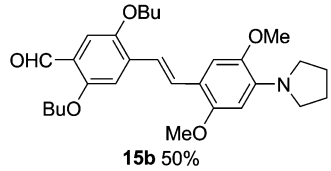
Table 1. Synthesis of the 4-Styrylbenzaldehydes



Phosphonate	ArCHO	Bromostilbenes	Styrylbenzaldehydes
8	 **7a**	 **10a** 87%	 **10b** 80%
8	 **5b**	 **11a** 91%	 **11b** 68%
8	 **7b**	 **12a** 94%	 **12b** 70%
9	 **5a**	 **13a** 92%	 **13b** 57%
9	 **5b**	 **14a** 92%	 **14b** 47%
9	 **7b**	 **15a** 88%	 **15b** 50%

Upon excitation at the lowest energy absorption maxima, the chromophores **MS 1–8** exhibit bright fluorescence at room temperature with a large Stokes shift from the relevant absorption maxima (see Table 3). The positions of the corresponding emission maxima are found to be independent of the excitation wavelength. Likewise, an excellent overlapping of the excitation spectra with the relevant lowest energy absorption maxima for the title chromophores **MS 1–8** was observed (see Figure 1a and 1b), thereby signifying the involvement of this photo-excited state for the occurrence of fluorescence. The effect of solvent polarity on the emission property of the present chromophores was found to be pronounced as compared to the absorption spectra (see Table 3). This observation is indicative of the fact that the photo–excited state of the concerned luminophores is markedly polar than the ground electronic state. The effect of solvent polarity on the emission properties is even more profound in case of the OPV derivatives (**MS 4–8**) compared to the styryl-analogues **MS 1–3** (see Table 3 and Figure 1c). The variation in the photoluminescent quantum yield of all of the title fluorophores was examined with the same set of solvents and is compiled in Table 3. The OPV derivatives, **MS 4–8**, exhibit brighter fluorescence in comparison with the first homologues, **MS 1–3** (see Table 3). The relative quantum yield of the title chromophores is, however, strongly dependent on the fluid medium, and an irregular alteration of the same with the solvent polarity is observed (see Table 3).

A comparison of the photophysical parameters of **MS 2** with that of its parents **HLB 1**[13d] and **N945L**[15a] shows that the ground state property of **MS 2** is comparable with that of **HLB 1**. Presumably, owing to the greater donation capability of the amino donor functionality in comparison with the methoxy donor, it has a dominant contribution in the respective ICT transition. However, a significant variation in the emission color was observed for **MS 2** in comparison with that of **HLB 1** and **N945L**. The chromophore **MS 2** exhibits a deep green emission at 533 nm in DCM that occurs at considerably longer

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Table 2. Selected ^{1}H NMR Chemical Shifts for MS 1−8[a]

compound	Py−H$^{6,6'}$[b]	Py−H$^{3,3'}$	Py−H$^{5,5'}$[c]	CH=CH[d]
MS 1	8.625 (d)	8.48 (s)	7.35−7.34	7.41 (d), 6.91 (d)
MS 2	8.635 (d)	8.48 (d)	7.44−7.43	7.75 (d), 7.05 (d)
MS 3	8.605 (d)	8.46 (s)	7.43−7.41	7.75 (d), 6.98 (d)
MS 4	8.695 (d)	8.56 (s)	7.42−7.40	7.50 (d), 7.47 (d), 7.14 (d), 7.00 (d)
MS 5	8.680 (d)	8.56 (s)	7.42−7.40	7.50 (d), 7.47 (d), 6.94 (d)
MS 6	8.675 (d)	8.52 (s)	7.46−7.45	7.80 (d), 7.28 (d), 7.20 (d), 7.10 (d)
MS 7	8.675 (d)	8.51 (s)	not resolved	7.80 (d), 7.37 (d), 7.21 (d)
MS 8	8.675 (d)	8.51 (s)	not resolved	7.80 (d), 7.49 (d), 7.32 (d), 7.20 (d)

[a]All spectra were recorded at 400 MHz working frequency in $CDCl_3$ at 298 ± 2 K. The resonances are reported in ppm with respect to the TMS signal. [b]$^3J_{HH}$ = 4 Hz except in **MS 5** for which J = 8 Hz. [c]Could be either doublet or doublet of doublet. [d]Coupling constant ($^3J_{HH}$) ≈ 16 Hz, for **MS 5** and **MS 6** one signal is overlapped with others and could not be separately detected. **MS 1−3** contain only two vinylic protons in their molecular structure.

wavelength than the emission due to **HLB 1** (497 nm) or **N945L** (450 nm). Addition of the amino functionality to **N945L** or two methoxy donors to **HLB 1** generates **MS 2**, which exhibits a significant weaker fluorescence compared to that of **N945L**, though the fluorescence quantum yields of **MS 2** and **HLB 1** are reasonably comparable. Hence, it can be said that presence of both the amino and the methoxy functionalities in same chromophore has a more profound effect on the emitting state compared to the ground state of the aforementioned luminophores.

The absorption and emission behavior of the OPVs **HLB 2**, **TM 6**, and **MS 4** follow an almost similar trend as the first homologues, viz., **HLB 1**, **N945L**, and **MS 2**, respectively. For a convenient discussion, the two phenyl rings of the OPV chromophores were named as ring A and ring B (see Chart 1). The hybrid chromophore **MS 4**, which comprises both the -NBu_2 and the -OMe functionalities in the same positions as in **HLB 2**[13h] and **TM 6**,[19a] absorbs at 413 nm (in DCM) due to an ICT and exhibits an orange-red emission (λ_{em} = 644 nm) with a very large Stokes shift (8685 cm^{-1}). Thus, like the first homologues, coexistence of the methoxy donors along with the dibutylamino groups in **MS 4** has very little influence on the absorption wavelength. The influence of methoxy donors is found to be rather dramatic on the fluorescence behavior of the relevant OPV chromophores. Compared to **HLB 2** and **TM 6**, the fluorophore **MS 4** emits at a considerably longer wavelength but with almost half photoluminescent quantum yield. In other words, both the approaches, viz., (a) attaching methoxy donors to **HLB 2** at ring B or (b) introducing amino donor to **TM 6** at ring B, render a significant bathochromic shift of the emission wavelength in the resultant chromophore but with the concomitant diminution of the fluorescence brightness.

One Photon Absorption and Emission Properties: (b) Position of Substituents. A careful analysis of the optical data presented in Table 3 reveals some interesting features. The OPV chromophores **MS 4**, **MS 6**, and **MS 7** were designed and synthesized in order to investigate the outcome of varying the position and number of alkoxy donors on the absorption and emission properties of the relevant chromophores. In **MS 4**, two methoxy donors were attached with ring B at the 2,5-positions along with the dibutylamino donor at the 4-position

Table 3. Summary of Optical Data of the Synthesized Chromophores (MS 1−8)

compound	solvent[a]	λ_{max} (nm)	ε (±500−1000)[b] (L mol^{-1} cm^{-1})	λ_{em}[c] (nm)	Φ_{em} (±0.1)[d]	$\Delta\bar{\nu}$[e] (cm^{-1})
MS 1	toluene	390		448	0.05	3320
	THF	393		485	0.09	4827
	DCM	396		498	0.09	5172
MS 2	toluene	392		472	0.09	4324
	THF	396		507	0.17	5529
	DCM	399	60000	533	0.20	6301
	MeCN	397		550	0.03	7007
MS 3	toluene	408		480	0.10	3677
	THF	410		516	0.18	5010
	DCM	414	84000	543	0.17	5738
	MeCN	408		560	0.04	6653
MS 4	toluene	409	114000	540	0.55	5931
	THF	409	100000	615	0.64	8190
	DCM	413	95000	644	0.37	8685
	MeCN	405		585	0.07	7597
MS 5	toluene	427		552	0.85	5303
	THF	426		630	0.72	7601
	DCM	430	122000	662	0.21	8150
	MeCN	428		603	0.17	6781
MS 6	toluene	436	116000	538	0.66	4348
	THF	437	99000	575	0.81	5492
	DCM	442	95000	598	0.65	5902
	MeCN	433		641	0.19	7494
MS 7	toluene	432	100400	550	0.63	4966
	THF	431	96000	591	0.62	6281
	DCM	435	87000	648	0.35	7556
	MeCN	430		650	0.03	7871
MS 8	toluene	445	131000	556	0.59	4486
	THF	445	100000	627	0.61	6523
	DCM	448	98500	660	0.23	7170
	MeCN	428		640	0.07	7740

[a]$E_T(30)$ values of the used solvents are as follows: toluene (33.9), THF (37.4), DCM (40.7), MeCN (45.6).[21] [b]Average of five data. In cases where no data are reported, this is due to low solubility. [c]The solutions were excited at the corresponding lowest energy absorption maxima. [d]Fluorescence relative quantum yield of the compound **MS 1** was measured using quinine sulfate (in 1 N H_2SO_4) as the reference (Φ_{em} = 0.545),[22] and those of the rest of the compounds (**MS 2−8**) were determined using DCM−Pyran as the reference in MeOH (Φ_{em} = 0.435).[23] Comparable result was obtained using fluorescein (in 0.1 N NaOH) as the standard substance also. Optically matched solutions (OD ≈ 0.05) of the samples and of the standards were excited at identical operating condition. Data is presented as an average of two measurements. [e]Stokes shift $\Delta\bar{\nu} = \bar{\nu}_{abs} - \bar{\nu}_{em}$.

(Chart 1). The alkoxy donors were moved to ring A (2,5-positions) in case of **MS 6** for which two butyloxy donors were used to aid in solubility instead of two methoxy donors as in **MS 4**, the total number of donor units being same for both the chromophores. The alkyl chain length in the alkoxy donors is not expected to alter the +I effect to a very significant extent. The absorption due to an intramolecular charge transfer in **MS 6** (442 nm in DCM) is shifted to longer wavelength by ca. 30 nm compared to that in **MS 4** (413 nm in DCM), and the reason behind this might probably be due to the greater extent of donor(alkoxy)−acceptor(pyridine) interaction in **MS 6** due to a smaller separation between the concerned functionalities. On the contrary, the emission spectrum of **MS 6** exhibits an almost 45 nm hypsochromic shift compared to **MS 4** in DCM,

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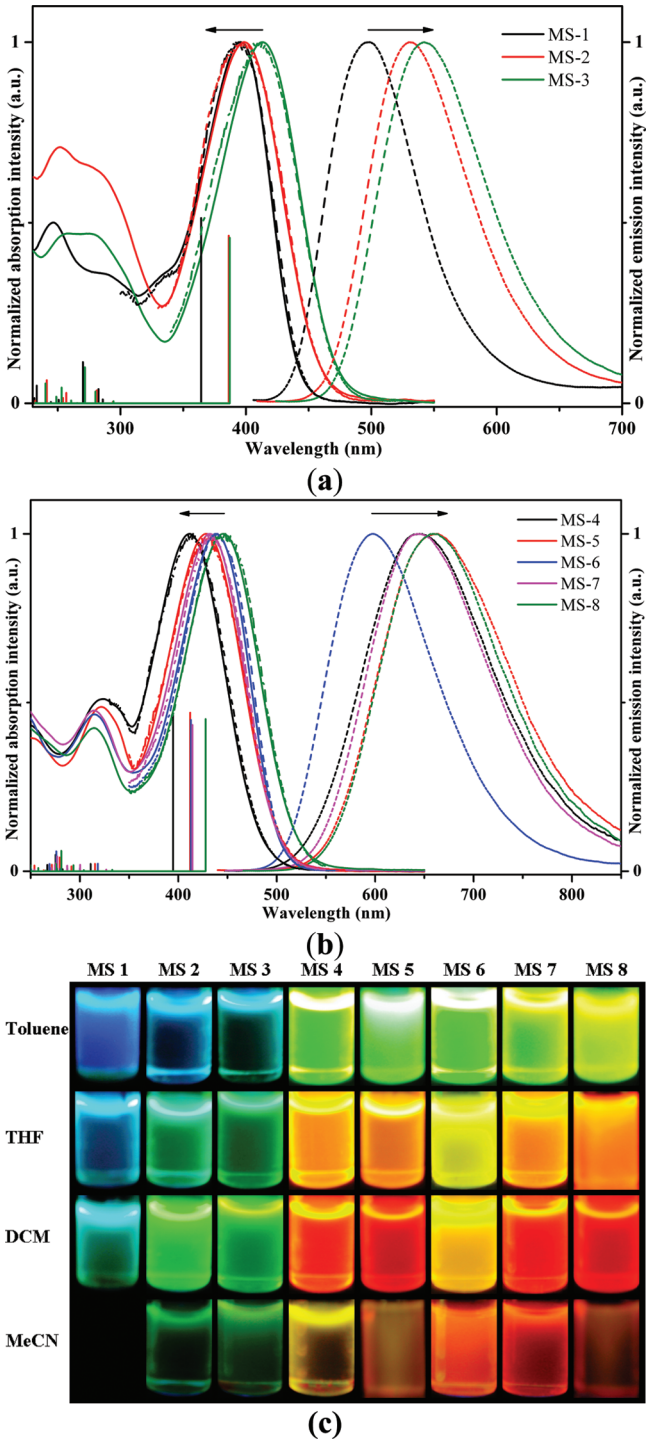

Figure 1. Normalized absorption (solid lines, concentration of the samples being ~1 × 10^{-5} M), emission (dashed lines), and excitation spectra (overlapped with the absorption spectra) together with the computed vertical excitation energies (stick lines) of (a) **MS 1–3** and (b) **MS 4–8** in DCM at 298 ± 2 K. All of the solutions were excited at the lowest energy absorption maxima. Heights of the vertical lines were adjusted so as to obtain viewing lucidity; the relative heights are however in scale. (c) Photographs showing photoluminescence behavior of the **MS 1–8** in four different solvents illuminated under an UV lamp (excitation 365 nm) in the dark.

and furthermore, the fluorescence quantum yield of **MS 6** is considerably larger than that of **MS 4** (Φ_{em} = 0.65 for **MS 6** and 0.37 for **MS 4** in DCM). The chromophores **MS 7** and **MS 8** bear the highest number of donor units among all of the compounds discussed in this article. Most surprisingly, despite attaching extra alkoxy donors with the ring B of **MS 6**, a further shift of the ICT absorption to the longer wavelength has not been induced but instead a hypsochromic shift of ca. 7 nm of the relevant band position is observed for **MS 7**. The emission properties of the luminophores **MS 4** and **MS 7** are almost similar except in MeCN in which the former exhibits yellow emission but the latter exhibits red emission (see Table 3 and Figure 1c).

Solid-State Emission of MS 5. Among all of the studied "push–pull" chromophores in the present work (**MS 1–8**), compound **MS 5** fluoresces even in the solid state. The solid-state absorption and emission spectra of the pertinent compound were recorded in dilute KBr matrix, and the relevant spectra are presented in Figure 2. The absorption

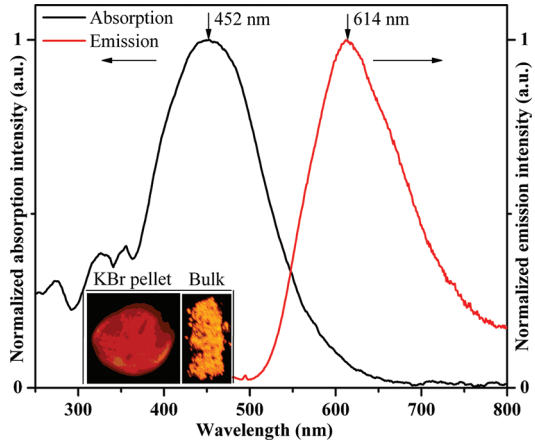

Figure 2. Solid-state absorption (black) and emission (red) spectra of **MS 5** at room temperature (KBr pellet, arbitrary concentration). The inset shows photographs of the relevant KBr pellet and bulk sample illuminated with a 365 nm UV lamp.

spectrum is characterized by a broad band centered at 442 nm that is slightly red-shifted with respect to the absorption maxima of the relevant dyad in the dissolved media (see Table 3). The bathochromic shift of the absorption maximum in condensed phase as compared to that of the solution state is presumably due an aggregation. When excited at the relevant absorption maximum, the chromophore **MS 5** exhibits orange emission with the maximum intensity at 614 nm (see Figure 2).

Computational Analysis. To gain insight into the effect of various substituents on the geometrical and electronic outcome of the 2,2′-bipyridine chromophores, density functional theory (DFT) and time-dependent DFT (TD-DFT) were applied on the synthesized compounds **MS 1–8** along with **HLB 1**, **N945L**, **HLB 2**, **TM 6**, and styryl- and bistyryl-derivatives without any donor substituent using the Gaussian09 program package.[24] Although the DFT analysis of **N945L** has already been reported,[15a] we have reproduced the same with our own computational setup for the purpose of ready comparison. A semiempirical calculation on **HLB 2** was earlier reported by Hernández and co-workers (named as **SY187**).[25] The geometry of all of the studied systems was optimized using the CAM-B3LYP exchange-correlation hybrid functional together with the 6-31+g(d) basis set imposing C_i symmetry constraint. All of the butyl chains of the OPV derivatives (**MS 4**, **MS 6**, and **MS 7**) were truncated to methyl groups in

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an attempt to reduce the number of basis functions and consequently to increase the computational speed. The relevant geometrical structures were modeled by applying the self-consistent reaction field (SCRF) under the polarizable continuum model (C-PCM) incorporating DCM as the solvent. For the purpose of ready comparison between the various computed parameters, an identical theoretical setup was maintained throughout the course of the computational investigations. The DFT-computed HOMO and LUMO frontier molecular orbitals (FMOs) of the chromophores **MS 1−8** are presented in Figure 3. A scrutiny on the computer-modeled

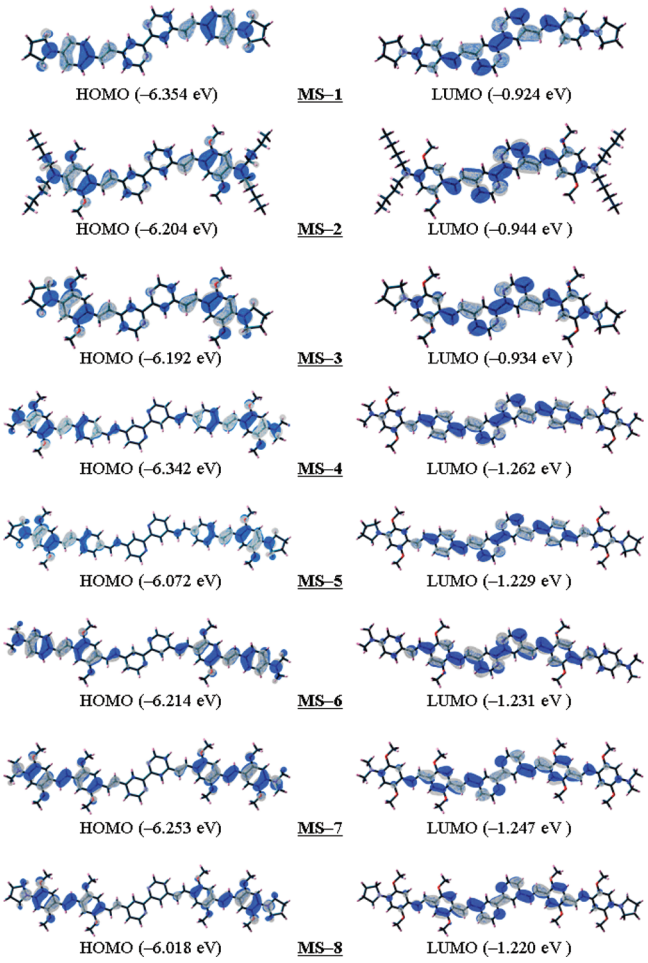

Figure 3. Isodensity plots of HOMO and LUMO frontier molecular orbitals of the bipyridine chromophores **MS 1−8** as computed by the CAM-B3LYP/6-31+g(d) level of theory (isodensity value = 0.02). The butyl chains of **MS 4** and **MS 6−8** were truncated to methyl groups.

structures of the studied systems reveals some common features such as almost coplanar structure of the systems that are devoid of any alkoxy functionality, out-of-plane displacement of the phenyl rings bearing the alkoxy substituents from the planes containing the pyridine ring and the C═C vinylic bonds, etc. Hence, these matters have not been individually addressed in this article.

An investigation on the electronic structures reveals that an almost similar type of localization and nature of HOMO and LUMO are retained among the individual homologues (see Figure 3), the only difference being in the energy of these FMOs, which in turn depend on the system architecture. The HOMO of the relevant chromophores is associated with the in-phase and out-of-phase π-bonding combination and consists of major coefficients at the phenyl rings containing the donor substituents and at the C═C vinylic bonds. On the contrary, the LUMO of the model structures stems from the π^*-type combination of the molecular orbitals (MOs), mainly contributed by the C═C bonds and the two pyridine rings along with a sizable coefficient on the C−C bond joining the two pyridine rings. The modulation of energy for the four occupied (HOMO−3, HOMO−2, HOMO−1, HOMO) and four virtual (LUMO, LUMO+1, LUMO+2, LUMO+3) molecular orbitals along with the corresponding computed HOMO−LUMO gap (E_g) upon alteration of the core architecture in the studied systems are presented in the Supporting Information. The HOMO−1 and HOMO occupied MOs of all of the studied systems constitute an almost degenerate couple. Such pairs in 4,4′-bis(styryl)-2,2′-bipyridine and 4,4′-bis(4-styryl)-2,2′-bipyridine, which are devoid of any donor functionality, are most stabilized among all of the model structures and are computationally estimated at −7.534/−7.480 and −6.936/−6.909 eV, respectively. A varying degree of destabilization of the HOMO−1 and HOMO occupied levels along with alteration of the HOMO−LUMO gap was observed upon introduction of the donor substituents to the 2,2′-bipyridine core skeleton (see Supporting Information). The consequence of conjugation length on the electronic structure of the bipyridine dyads is evidently comprehended in the computer-modeled structures. For example, expansion of conjugation from **MS 3** to **MS 5** results in destabilization of the HOMO by 0.108 eV and a sizable shrinking of the HOMO−LUMO gap by 0.407 eV with respect to **MS 3**.

The various vertical Franck−Condon electronic excitations were computed by the TD-DFT formalism in order to comprehend the nature of electronic transitions responsible for appearance of the absorption bands in the relevant electronic spectra. Some representative excited states for **MS 1−8** and the computer-generated absorption spectra of the studied systems are presented in the Supporting Information. The computed vertical excitations for **MS 1−8** in DCM are shown in Figure 1a and b. An initial attempt to compute the excited states (TD-DFT) using the B3LYP hybrid functional has resulted in large overestimation of the absorption bands, mostly for the OPV analogues. In particular, the well-celebrated TD-DFT method is often known to produce flawed results in the case of computation on the excited states of molecules with extended π-systems and those that involve a charge transfer character.[26] This method (TD-DFT) is also known to be sensitive to the functional to gain the correct long-range $1/R$ dependence on the donor−acceptor distance in the π-expanded systems.[26] Configuration Interaction Singles (CIS) is a promising method to compute the excited states of such systems, but our attempts to calculate the absorption spectra of the present OPV chromophores at this level have not improved the situation. This has prompted us to use the recently developed coulomb-attenuated long-range corrected version of B3LYP, i.e., CAM-B3LYP, hybrid functional, which has turned out to be very promising as this functional recovers the long-range $1/R$ behavior.[27]

A fair agreement between the computed vertical excitations and the experimentally observed absorption maxima is observed for the studied systems (see Figure 1a and b). The lowest energy intense absorption band in all of the cases is due to the involvement of two excited states, viz., HOMO−1 → LUMO and HOMO → LUMO+1 excitations with high oscillator

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strength ($f > 1$) indicating a $\pi \rightarrow \pi^*$ ICT from the donor-based molecular orbitals to the pyridine (acceptor)-centered molecular orbitals. The HOMO(A_u) → LUMO(A_u) excitation in all of the studied systems is symmetrically forbidden and does not contribute to the electronic absorption spectra in the relevant bipyridine dyads. The scenario of the computed electronic excitations thereby essentially points out the "push−pull" architecture of the pertinent systems. Unfortunately, ∼15 nm bathochromic shift of the ICT absorption maximum of **MS 3** in comparison with **MS 2** could not be reproduced in our computational setup. Interestingly, the ∼18 nm red-shift of the ICT absorption maximum for **MS 6** was computed in comparison with **MS 4**, very similar to the experimentally observed ∼30 nm bathochromic shift upon identical alteration of the donor position (see Table 3). However, the experimentally observed ∼7 nm hypsochromic shift of the ICT band maximum upon increment of the number of alkoxy donors from **MS 6** to **MS 7** could not be reproduced.

Thermal Stability. Thermal durability is one of the most significant and essential parameters for custom-tailored applications of the bench-top-synthesized compounds. The thermal decay/weight loss of compounds **MS 1−8** was examined by heating the solid samples in an analyzer under a flow of nitrogen. Thermal weight loss behavior of the chromophores **MS 3**, **MS 5**, and **MS 6−8** are shown in Figure 4, which depicts

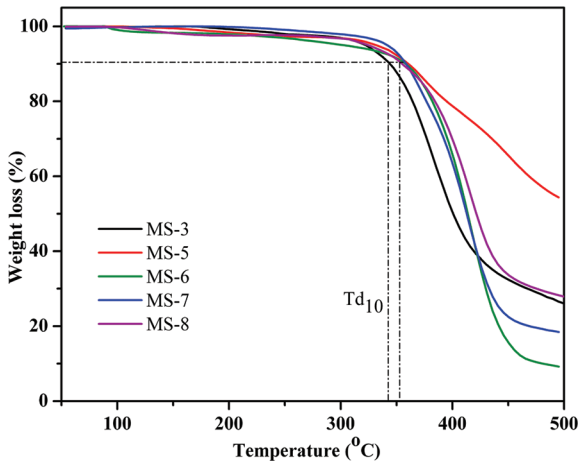

Figure 4. Thermogravimmetric Behavior of **MS 3**, **MS 5**, and **MS 6−8**.

very high thermal stability of the relevant "push−pull" chromophores. The 10% weight loss temperature (T_{d10}) for these chromophores is evidently high (∼350 °C) as shown in Figure 4. No significant weight loss occurs even up to 250 °C. However, the T_{d10} value for compounds **MS 1−2** and **MS 4** are found to be relatively low (ca. 150 °C).

CONCLUSION

In summary, a series of 4,4′-π-conjugated-2,2′-bipyridine dyads having a D-π-A-A-π-D architecture were synthesized wherein the 2,2′-bipyridine heterocycle acts as the central acceptor core to join the donor termini through olefinic spacers. The photophysical properties (absorption and emission) of the synthesized chromophores are governed by the intramolecular charge separation from the donor end-capping functionalities to the pyridine acceptor heterocycle. This observation is in line with the photophysics of previously reported related dyes. The emitting state of the fluorophores is substantially more polar than the ground electronic state, which was affirmed by the large solvent-sensitive photoluminescent behavior of the synthesized compounds. The absorptive and emissive nature of the present chromophores are enormously dependent on the conjugation backbone, i.e., the nature, position, and number of donor functionalities, the parameters which act as the function of their photophysical outcome. The computational analyses of the absorption properties of the synthesized chromophores clearly depict an alteration of the various occupied and virtual energy levels with the structure of the synthesized chromophores and is in fair agreement with the variation trend of the experimentally observed absorption spectra.

In this work, we have demonstrated optical properties of 4,4′-π-conjugated-2,2′-bipyridine dyes that were fabricated with heterodonor functionalities. We have shown how simple modification of the π-skeleton of these dyes modulates their fluorescence behavior. For example, out of the eight dye stuffs described in this article, the compound, **MS 5** fluoresces even in the condensed phase ,which is one of the prerequisites for possible application in light-emitting devices. Thus, changing the amino donor from open chain dibutylamino in **MS 4** to the cyclic pyrrolidine donor in **MS 5** results in this differing photophysical behavior. Although the 4,4′-π-conjugated-2,2′-bipyridine derivatives were extensively studied in terms of devising nonlinear optical and solar energy harvesting materials, our systematic study on the photophysical properties of the heterodonor systems in comparison with the parent chromophores bearing alike donor functionalities approaches a structure−function relationship that would be useful for choosing the proper material for practical applications. Accordingly, the findings of the present study in conjunction with the photophysics of the earlier reported parent dye molecules construct a library of such systems in which the present investigation finds some notable differences in the fluorescence responses compared to the parent molecules functionalized with only one kind of donor subchromophores. The present work reveals that the coexistence of both the alkoxy and amino functionalities in the same phenyl ring modulates the emitting state of **MS 2** and **MS 4**, which exhibit considerable bathochromic shifted fluorescence with respect to the reported chromophores having either alkoxy (**N945L**, **TM 6**) or amino (**HLB 1-2**) donor groups. Furthermore, moving the alkoxy donors from ring B (**MS 4**) to ring A (**MS 6**) results in a large bathochromic shift of the absorption wavelength presumably due to the enhanced participation of the alkoxy groups in the charge transfer process when placed in ring A rather than in ring B. The introduction of additional alkoxy donor functionalities does not induce further bathochromic shift of the absorption maxima. Furthermore, it is firmly believed that the transition metal complexes of the present neutral bipyridine chromophores would exhibit exciting linear and nonlinear optical responses, and this work is presently under progress in our laboratory.

EXPERIMENTAL SECTION

***N,N*-Dibutylaniline (4a).** A mixture of aniline (19 mL, 200 mmol), 1-bromo butane (65 mL, 600 mmol), and Na_2CO_3 (84 g, 800 mmol) in 100 mL of 90:10 v/v DMF/*N*-methylpyrrolidinone (NMP) was heated at 120 °C for 24 h. The reaction mixture was then cooled to room temperature and filtered to remove the insoluble material. The precipitate was washed with ethyl acetate, and the combined filtrate was evaporated to dryness. Water was then added, and the

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aqueous phase was extracted with ethyl acetate. After a silica gel filtration using hexane as the mobile phase, the pure compound was obtained as a pale yellow liquid. Yield: 35.3 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.21 (unresolved, 2H), 6.68 (unresolved, 3H), 3.29 (t, 4H), 1.58 (unresolved, 4H), 1.41−1.35 (m, 4H), 1.00 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.2, 115.1, 111.7, 50.8, 29.4, 20.4, 14.0. LC−MS (positive mode): m/z 206 $(M + H)^+$. Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.83; H, 11.33; N, 6.84.

_N,N_-Dibutyl-2,5-dimethoxyaniline (4b). This compound was synthesized using the same procedure as described for compound **4a**. 2,5-Dimethoxy aniline (**3b**, 30.6 g, 200 mmol) was used instead of aniline (**3a**), and the reaction time was 72 h at 120 °C. The black crude liquid was subjected to silica gel filtration using hexane as the eluant to obtain the pure product **4b** as a light-sensitive pale yellow liquid. Yield: 38.7 g (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (d, J = 8 Hz, 1H), 6.54 (d, $^4J_{HH}$ = 4 Hz, 1H), 6.46−6.43 (dd, J = 8 Hz, $^4J_{HH}$ = 4 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.08 (t, 4H), 1.45 (p, 4H), 1.28 (sextet, 4H), 0.88 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 147.9, 141.3, 112.8, 108.7, 104.7, 56.2, 55.5, 52.4, 26.9, 20.5, 14.1. LC−MS (positive mode): m/z 266 $(M + H)^+$. Anal. Calcd for $C_{16}H_{27}NO_2$: C, 72.41; H, 10.25; N, 5.28. Found: C, 72.47; H, 10.11; N, 5.32.

4-(Dibutylamino)benzaldehyde (5a). $POCl_3$ (5.5 mL, 60 mmol) was slowly added to a DMF (20 mL, excess) solution of *N,N*-dibutyl aniline (**4a**, 10.25 g, 50 mmol) with cooling in an ice bath under an inert atmosphere. The resulting orange-red viscous liquid was then stirred at this temperature for 15 min, slowly warmed to room temperature, and then heated at 90−95 °C for 7 h. The dark reaction mixture was then cooled in an ice bath and carefully quenched with water, followed by neutralization with aqueous Na_2CO_3 solution. The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and brine, dried (anhydrous Na_2SO_4), and evaporated. Chromatographic purification of the crude mixture in a silica gel (100−200 mesh) column eluting with EtOAc/Hexane 15:85 v/v gave the product **5a** as a yellow viscous liquid. Yield: 11.16 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.69 (d, J = 8 Hz, 2H), 6.64 (d, J = 8 Hz, 2H), 3.35 (t, 4H), 1.60 (p, 4H), 1.36 (hextet, 4H), 0.97 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 152.6, 132.2, 124.5, 110.7, 50.8, 29.3, 20.3, 20.25, 13.9. IR (neat, cm^{-1}): υ_{max} 1680 (>C═O). LC−MS (positive mode): m/z 234 $[M + H]^+$. Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 6.00. Found: C, 77.27; H, 9.84; N, 6.12.

4-(Dibutylamino)-2,5-dimethoxybenzaldehyde (5b). This compound was synthesized using the same procedure as described for **5a**. *N,N*-Dibutyl-2,5-dimethoxyaniline (**2b**, 13.25 g, 50 mmol) was used instead of *N,N*-dibutyl aniline (**2a**). Reaction time at 90−95 °C: 4 h. The product **5b** was isolated as an orange-yellow viscous liquid after silica gel (100−200 mesh) filtration of the crude with EtOAc/Hexane 20:80 v/v as the mobile phase. Yield: 12.60 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.20 (s, 1H), 7.25 (s, 1H), 6.27 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.30 (t, 4H), 1.55 (p, 4H), 1.31 (hextet, 4H), 0.90 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 158.6, 147.9, 145.3, 115.9, 110.1, 100.6, 55.98, 55.90, 52.2, 29.8, 20.4, 14.0. IR (neat, cm^{-1}): υ_{max} 1660 (>C═O). LC−MS (positive mode): m/z 294 $[M + H]^+$. Anal. Calcd for $C_{17}H_{27}NO_3$: C, 69.59; H, 9.28; N, 4.77. Found: C, 69.51; H, 9.33; N, 4.70.

1-Phenylpyrrolidine (6a). A mixture of aniline (4.6 mL, 50 mmol), 1,4-dibromobutane (6.5 mL, 55 mmol), and K_2CO_3 (28 g, 200 mmol) in 90:10 v/v DMF/*N*-methylpyrrolidinone (NMP) was heated at 120 °C for 24 h after which it was cooled to room temperature and filtered. The precipitated solid was washed with ethyl acetate, and the combined filtrate was evaporated to dryness. Water was then added, and the aqueous phase was extracted with ethyl acetate. The crude product was purified on short silica gel column eluting with EtOAc/Hexane 1:99 v/v to afford the pure product **6a** as a yellow light-sensitive liquid. Yield: 4.7 g (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.25 (unresolved, 2H), 6.70−6.61 (m, 3H), 3.32 (unresolved, 4H), 2.04 (unresolved, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 129.2, 115.6, 111.8, 47.7, 25.5. LC−MS (positive mode): m/z 148 $(M + H)^+$. Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.48; H, 9.04; N, 9.48.

1-(2,5-Dimethoxyphenyl)pyrrolidine (6b). This compound was prepared using the same procedure as described for the synthesis of compound **6a**; 7.6 g (50 mmol) of 2,5-dimethoxy aniline was used instead of aniline, and the reaction mixture was heated at 120 °C for 48 h. Silica gel filtration using EtOAc/Hexane 5:95 v/v as the mobile phase afforded the pure compound **6b** as a yellow light-sensitive liquid. Yield: 7.9 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, J = 8 Hz, 1H), 6.38 (d, $^4J_{HH}$ = 4 Hz, 1H), 6.34−6.31 (dd, J = 8 Hz, $^4J_{HH}$ = 4 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 33.2 (unresolved, 4H), 19.4 (unresolved, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 144.8, 141.1, 113.0, 103.1, 101.6, 56.6, 55.5, 50.4, 24.5. LC−MS (positive mode): m/z 208 $(M + H)^+$. Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.41; H, 8.23; N, 6.73.

4-(Pyrrolidin-1-yl)benzaldehyde (7a). This compound was synthesized using the same procedure as described for **5a**. 1-Phenylpyrrolidine (**6a**, 7.35 g, 50 mmol) was used instead of *N,N*-dibutyl aniline (**4a**). Reaction time at 90−95 °C: 6−7 h. Column chromatographic (silica gel, 100−200 mesh) purification of the crude product using EtOAc/Hexane 20:80 v/v as the eluent afforded the desired product **7a** as a white crystalline solid. Yield: 7.26 g (83%). Mp: 81−83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.73 (d, J = 8 Hz, 2H), 6.57 (d, J = 8 Hz, 2H), 3.41−3.37 (m, 4H), 2.07−2.04 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 152.0, 132.1, 124.9, 111.2, 47.7, 25.4. IR (KBr, cm^{-1}): υ_{max} 1674 (>C═O). LC−MS (positive mode): m/z 176 $[M + H]^+$. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.45; H, 7.39; N, 8.07.

2,5-Dimethoxy-4-(pyrrolidin-1-yl)benzaldehyde (7b). This compound was synthesized using the same procedure as described for **5a**. 1-(2,5-Dimethoxyphenyl)pyrrolidine (**6b**, 10.35 g, 50 mmol) was used instead of *N,N*-dibutyl aniline (**4a**). Reaction time at 90−95 °C: 7−8 h. The crude product was purified by silica gel (100−200 mesh) column eluting with EtOAc/Hexane 20:80 v/v as the mobile phase to obtain the pure aldehyde **7b** a light-sensitive cream colored solid. Yield: 10.34 g (88%). Mp: 120−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (s, 1H), 7.23 (s, 1H), 6.00 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.55 (unresolved, 4H), 1.93 (unresolved, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7, 159.5, 146.7, 142.9, 113.8, 110.1, 96.2, 56.4, 55.8, 50.7, 25.5. IR (KBr, cm^{-1}): υ_{max} 1639 (>C═O). LC−MS (positive mode): m/z 236 $[M + H]^+$. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.28; H, 7.25; N, 6.11.

(*E*)-4-(4-(Pyrrolidin-1-yl)styryl)bromobenzene (10a). Solid potassium *tert*-butoxide (1.68 g, 15 mmol) was added at once to an ice-cooled THF solution (30 mL) containing 3.68 g of phosphonate **8** (12 mmol) and 1.75 g of aldehyde **7a** (10 mmol) under an inert atmosphere. The resulting slurry was warmed to room temperature and stirred for 60 min before the reaction was quenched with water. The precipitated yellow solid was collected by filtration, washed several times with water, and dried in air. It was re-dissolved in dichloromethane (ca. 600 mL), and the solvent was rotavaporated to ca. 15 mL and filtered to obtain the pure product **10a** as yellow solid. Yield: 2.85 g (87%). Mp: >200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 7.03 (d, J = 16 Hz, 1H), 6.81 (d, J = 16 Hz, 1H), 6.55 (d, J = 8 Hz, 2H), 3.33 (unresolved, 4H), 2.02 (unresolved, 4H). ^{13}C NMR was not possible because of low solubility. LC−MS (positive mode): m/z 328 $(M)^+$, 330 $(M + 2H)^+$. Anal. Calcd for $C_{18}H_{18}BrN$: C, 65.86; H, 5.53; N, 4.27. Found: C, 65.69; H, 5.48; N, 4.30.

(*E*)-4-(4-(Dibutylamino)-2,5-dimethoxystyryl)bromobenzene (11a). Under nitrogen, solid potassium *tert*-butoxide (1.68 g, 15 mmol) was added all at once to a THF solution (30 mL) containing 3.68 g of phosphonate **8** (12 mmol) and 2.93 g of aldehyde **5b** (10 mmol) pre-cooled at 0 °C. The ice bath was removed, and the reaction mixture was allowed to stir at room temperature for 60 min. It was subsequently quenched with water and then extracted with dichloromethane. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness. Purification of the crude product through column chromatography (silica gel, 100−200 mesh) using EtOAc/Hexane 5:95 v/v as the eluent afforded the

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product **11a** as dark yellow solid. Yield: 4.06 g (91%). Mp: 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.37 (m, 5H), 7.06 (s, 1H), 6.89 (d, J = 16 Hz, 1H), 6.50 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.16 (t, 4H), 1.51 (p, 4H), 1.33 (m, 4H), 0.90 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 147.4, 141.4, 137.4, 131.6, 127.7, 125.0, 124.1, 120.4, 118.4, 110.3, 105.2, 52.3, 29.3, 20.6, 14.1. LC−MS (positive mode): m/z 446 $(M)^+$, 448 $(M + 2H)^+$. Anal. Calcd for $C_{24}H_{32}BrNO_2$: C, 64.57; H, 7.23; N, 3.14. Found: C, 64.43; H, 7.16; N, 3.16.

(*E*)-4-(2,5-Dimethoxy-4-(pyrrolidin-1-yl)styryl)bromobenzene (12a). This compound was prepared using the same procedure as described for **11a** using 3.68 g of phosphonate **8** (12 mmol), 2.35 g of aldehyde **7b** (10 mmol), and 1.68 g of potassium *tert*-butoxide (15 mmol) in 30 mL of THF. Column chromatographic purification on silica gel (100−200 mesh) using EtOAc/Hexane 20:80 v/v as the mobile phase afforded the product **12a** as fluorescent yellow needles. Yield: 3.65 g (94%). Mp: 128−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−36 (m, 5H), 7.07 (s, 1H), 6.85 (d, J = 16 Hz, 1H), 6.29 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.41 (unresolved, 4H), 1.96 (unresolved, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 144.1, 141.1, 137.7, 131.6, 127.6, 124.2, 123.5, 120.0, 115.3, 110.8, 99.6, 56.9, 56.4, 50.5, 25.1. LC−MS (positive mode): m/z 388 $(M)^+$, 390 $(M + 2H)^+$. Anal. Calcd for $C_{20}H_{22}BrNO_2$: C, 61.86; H, 5.71; N, 3.61. Found: C, 62.01; H, 5.64; N, 3.55.

(*E*)-2,5-Dibutoxy-4-(4-(dibutylamino)styryl)bromobenzene (13a). This compound was prepared using the same procedure as described for **11a** using 2.3 g of phosphonate **7** (5 mmol), 1.1 g of aldehyde **5a** (4.8 mmol), and 0.7 g of potassium *tert*-butoxide (6 mmol) in 25 mL of THF. The product **13a** was isolated as fluorescent yellow solid after column chromatography on silica gel (100−200 mesh) using EtOAc/Hexane 5:95 v/v as the mobile phase. Yield: 2.34 g (92%). Mp: 84−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8 Hz, 2H), 7.16 (d, J = 16 Hz, 1H), 7.12 (s, 1H), 7.06 (s, 1H), 7.02 (d, J = 16 Hz, 1H), 6.54 (d, J = 8 Hz, 2H), 4.05 (t, 2H), 3.95 (t, 2H), 3.30 (t, 4H), 1.82 (p, 4H), 1.63−1.52 (m, 8H), 1.36 (t, 4H), 1.03−0.96 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 149.9, 147.9, 129.6, 127.8, 124.9, 117.8, 111.6, 111.2, 110.3, 70.0, 69.3, 50.8, 31.5, 29.5, 20.4, 19.4, 14.0. LC−MS (positive mode): m/z 531 $(M)^+$, 533 $(M + 2H)^+$. Anal. Calcd for $C_{30}H_{44}BrNO_2$: C, 67.91; H, 8.36; N, 2.64. Found: C, 68.02; H, 8.25; N, 2.69.

(*E*)-2,5-Dibutoxy-4-(4-(dibutylamino)-2,5-dimethoxystyryl)bromobenzene (14a). This compound was prepared using the same procedure as described for **11a** using 2.3 g of phosphonate **7** (5 mmol), 1.4 g of aldehyde **5b** (4.8 mmol), and 0.7 g of potassium *tert*-butoxide (6 mmol) in 25 mL of THF. The product **14a** was isolated as yellow solid after chromatographic purification on silica gel stationary phase (100−200 mesh) using EtOAc/Hexane 5:95 v/v as the mobile phase. Yield: 2.61 g (92%). Mp: 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 16 Hz, 1H), 7.26 (d, J = 16 Hz, 1H), 7.15 (s, 1H), 7.10 (s, 1H), 7.07 (s, 1H), 6.51 (s, 1H), 4.05 (t, 2H), 3.96 (t, 2H), 3.86−3.85 (m, 6H), 3.15 (t, 4H), 1.85−1.78 (m, 4H), 1.60−1.43 (m, 8H), 1.29 (m, 4H), 0.99 (t, 6H), 0.91 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 150.9, 149.9, 147.6, 141.1, 127.8, 123.9, 120.8, 119.4, 117.9, 111.7, 110.9, 110.5, 105.4, 70.0, 69.3, 56.5, 56.3, 52.4, 31.5, 29.4, 20.6, 19.4, 19.3, 14.0, 13.9. LC−MS (positive mode): m/z 590 $(M)^+$, 592 $(M + 2H)^+$. Anal. Calcd for $C_{32}H_{48}BrNO_4$: C, 65.07; H, 8.19; N, 2.37. Found: C, 65.10; H, 8.08; N, 2.43.

(*E*)-2,5-Dibutoxy-4-(2,5-dimethoxy-4-(pyrrolidin-1-yl)styryl)bromobenzene (15a). This compound was synthesized by the same procedure as described for **11a** using 2.3 g of phosphonate **7** (5 mmol), 1.1 g of aldehyde **7b** (4.8 mmol), and 0.7 g of potassium *tert*-butoxide (6 mmol) in 25 mL of THF. Chromatographic purification using silica gel stationary phase (100−200 mesh) and EtOAc/Hexane 10:90 v/v as the mobile phase afforded the product **15a** as fluorescent yellow solid. Yield: 2.25 g (88%). Mp: 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 16 Hz, 1H), 7.20 (d, J = 16 Hz, 1H), 7.15 (s, 1H), 7.10 (s, 1H), 7.06 (s, 1H), 6.30 (s, 1H), 4.05 (t, 2H), 3.96 (t, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.41 (unresolved, 4H), 1.95 (unresolved, 4H), 1.81 (p, 4H), 1.56 (m, 4H), 1.00 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 150.8, 149.9, 144.2, 140.8, 128.0, 124.0, 119.2, 117.9, 116.3, 111.4, 110.8, 110.4, 99.8, 70.0, 69.4, 56.8, 56.5, 50.5, 31.5, 25.1, 19.4, 19.3, 14.0. LC−MS (positive mode): m/z 532 $(M)^+$, 534 $(M + 2H)^+$. Anal. Calcd for $C_{28}H_{38}BrNO_4$: C, 63.15; H, 7.19; N, 2.63. Found: C, 63.21; H, 7.22; N, 2.68.

(*E*)-4-(4-(Pyrrolidin-1-yl)styryl)benzaldehyde (10b). A solution of bromostilbene **10a** (0.98 g, 3 mmol) in 110 mL of THF was cooled to −40 °C, and then 2.2 mL of 1.6 M *n*BuLi (3.6 mmol) was added dropwise. The heterogeneous mixture was stirred at this temperature for 60 min, and 0.4 mL of dry DMF (5 mmol) was subsequently added followed by stirring at this temperature for additional 60 min. The cooled reaction mixture was then slowly warmed to room temperature, quenched with saturated ammonium chloride solution, and extracted with dichloromethane. The organic layer was washed twice with water and then with brine, dried (Na_2SO_4), and evaporated to dryness. The crude product was purified by column chromatography on silica gel (100−200 mesh) using dichloromethane as the mobile phase to obtain the pure aldehyde **10b** as an orange yellow solid. Yield: 0.66 g (80%). Mp: >200 °C. IR (KBr, cm^{-1}): υ_{max} 1691 (>C═O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.83 (d, J = 8 Hz, 2H), 7.60 (d, J = 8 Hz, 2H), 7.43 (d, J = 8 Hz, 2H), 7.22 (d, J = 16 Hz, 1H), 6.92 (d, J = 16 Hz, 1H), 6.57 (d, J = 8 Hz, 2H), 3.33 (unresolved, 4H), 1.58 (unresolved, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 148.1, 144.8, 134.3, 132.9, 130.3, 129.4, 128.4, 126.2, 121.9, 111.8, 47.6, 25.5. LC−MS (positive mode): m/z 278 $(M + H)^+$. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. C, 88.23; H, 6.88; N, 5.12.

(*E*)-4-(4-(Dibutylamino)-2,5-dimethoxystyryl)benzaldehyde (11b). This compound was synthesized by the same procedure as described for aldehyde **10b** using bromostilbene **11a** (1.34 g, 3 mmol), 1.6 M *n*BuLi (2.2 mL, 3.6 mmol), and DMF (0.4 mL, 5 mmol) in 20 mL of THF was used instead. Chromatographic purification using silica gel stationary phase (100−200 mesh) and EtOAc/Hexane 10:90 v/v mobile phase rendered the aldehyde **11b** as a vermillion-red gummy mass. Yield: 0.81 g (68%). IR (KBr, cm^{-1}): υ_{max} 1695 (>C═O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.84 (d, J = 8 Hz, 2H), 7.65 (d, J = 8 Hz, 2H), 7.61 (d, J = 16 Hz, 1H), 7.09 (s, 1H), 7.01 (d, J = 16 Hz, 1H), 6.49 (s, 1H), 3.87 (unresolved, 6H), 3.18 (t, 4H), 1.52−1.47 (p, 4H), 1.33−1.26 (m, 4H), 0.91 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 152.3, 147.8, 144.8, 142.2, 134.6, 130.2, 127.0, 126.5, 124.6, 117.6, 110.5, 104.6, 56.40, 56.35, 52.2, 29.4, 20.5, 14.1. LC−MS (positive mode): m/z 396 $(M + H)^+$. Anal. Calcd for $C_{25}H_{33}NO_3$: C, 75.91; H, 8.41; N, 3.54. Found: C, 76.09; H, 8.35; N, 3.58.

(*E*)-4-(2,5-Dimethoxy-4-(pyrrolidin-1-yl)styryl)benzaldehyde (12b). This compound was synthesized by the same procedure as described for aldehyde **10b** using bromostilbene **12a** (1.16 g, 3 mmol), 1.6 M *n*BuLi (2.2 mL, 3.6 mmol), and DMF (0.4 mL, 5 mmol) in 20 mL of THF. Purification of the crude by column chromatography using silica gel (100−200 mesh) and EtOAc/Hexane 10:90 v/v mobile phase afforded the aldehyde **12b** as a vermillion-orange solid. Yield: 0.71 g (70%). Mp: 120−122 °C. IR (KBr, cm^{-1}): υ_{max} 1689 (>C═O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.82 (d, J = 8 Hz, 2H), 7.64−7.59 (m, 3H), 7.09 (s, 1H), 6.95 (d, J = 16 Hz, 1H), 6.26 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.44 (unresolved, 4H), 1.96 (unresolved, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 153.1, 145.1, 143.9, 141.8, 134.3, 130.3, 127.2, 126.3, 123.0, 114.6, 111.0, 99.1, 57.0, 56.3, 50.5, 25.2. LC−MS (positive mode): m/z 338 $(M + H)^+$. Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.62; H, 6.84; N, 4.13.

(*E*)-2,5-Dibutoxy-4-(4-(dibutylamino)styryl)benzaldehyde (13b). This compound was synthesized by the same procedure as described for aldehyde **10b** using bromostilbene **13a** (1.6 g, 3 mmol), 1.6 M *n*BuLi (2.2 mL, 3.6 mmol), and DMF (0.4 mL, 5 mmol) in 20 mL of THF. Chromatographic purification of the crude product on silica gel (100−200 mesh) using EtOAc/Hexane 5:95 v/v as the eluent afforded the aldehyde **13b** as a thick red gum. Yield: 0.82 g (57%). IR (KBr, cm^{-1}): υ_{max} 1672 (>C═O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.44 (s, 1H), 7.43 (d, J = 8 Hz, 2H), 7.31 (s, 1H), 7.23 (d, J = 16 Hz, 1H), 7.16 (s, 1H), 6.65 (d, J = 8 Hz, 2H), 4.13 (t, 2H), 4.03 (t, 2H), 3.32 (t, 4H), 1.86−1.83 (m, 4H), 1.59−1.53 (m, 8H), 1.41−1.37 (m, 4H), 1.04−0.96 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.0,

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156.5, 150.3, 148.3, 135.8, 132.7, 128.4, 124.4, 123.2, 117.4, 111.6, 110.0, 109.6, 68.9, 68.7, 50.8, 31.4, 29.5, 20.4, 19.4, 14.0. LC−MS (positive mode): m/z 481 $(M + H)^+$. Anal. Calcd for $C_{31}H_{45}NO_3$: C, 77.62; H, 9.46; N, 2.92. Found: C, 77.51; H, 9.42; N, 3.00.

(*E*)-2,5-Dibutoxy-4-(4-(dibutylamino)-2,5-dimethoxystyryl)-benzaldehyde (14b). This compound was synthesized by the same procedure as described for aldehyde **10b** using bromostilbene **14a** (1.8 g, 3 mmol), 1.6 M *n*BuLi (2.2 mL, 3.6 mmol), and DMF (0.4 mL, 5 mmol) in 20 mL of THF. The crude product was subjected to column chromatography on silica gel (100−200 mesh) using EtOAc/Hexane 5:95 v/v as the mobile phase to afford the aldehyde **14b** as a thick red gum. Yield: 0.76 g (47%). IR (KBr, cm^{-1}): υ_{max} 1674 (>C═O). ^1H NMR (400 MHz, $CDCl_3$): δ 10.42 (s, 1H), 7.58 (d, J = 16 Hz, 1H), 7.55 (d, J = 16 Hz, 1H), 7.30 (s, 1H), 7.19 (s, 1H), 7.12 (s, 1H), 6.50 (s, 1H), 4.12 (t, 2H), 4.02 (t, 2H), 3.86 (s, 6H), 3.18 (t, 4H), 1.83 (p, 4H), 1.58−1.48 (m, 8H), 1.31 (m, 4H), 1.00 (t, 6H), 0.91 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 156.4, 152.2, 150.5, 147.2, 141.9, 135.7, 126.9, 123.5, 120.2, 118.5, 110.6, 110.0, 109.9, 104.7, 68.8, 68.7, 56.4, 56.2, 52.2, 31.4, 31.3, 29.4, 20.5, 19.5, 19.3, 14.1, 14.0, 13.9. LC−MS (positive mode): m/z 541 $(M + H)^+$. Anal. Calcd for $C_{33}H_{49}NO_5$: C, 73.43; H, 9.15; N, 2.60. Found: C, 73.57; H, 9.09; N, 2.53.

(*E*)-2,5-Dibutoxy-4-(2,5-dimethoxy-4-(pyrrolidin-1-yl)styryl)-benzaldehyde (15b). This compound was synthesized by the same procedure as described for aldehyde **10b** using bromostilbene **15a** (1.6 g, 3 mmol), 1.6 M *n*BuLi (2.2 mL, 3.6 mmol), and DMF (0.4 mL, 5 mmol) in 20 mL of THF. Purification of the crude product by silica gel (100−200 mesh) column chromatography using EtOAc/Hexane 10:90 v/v as the mobile phase led to the aldehyde **15b** as a vermillion-orange solid. Yield: 0.72 g (50%). Mp: 103−105 °C. IR (KBr, cm^{-1}): υ_{max} 1670 (>C═O). ^1H NMR (400 MHz, $CDCl_3$): 10.42 (s, 1H), 7.58 (d, J = 16 Hz, 1H), 7.30 (d, J = 16 Hz, 1H), 7.29 (s, 1H), 7.19 (s, 1H), 7.12 (s, 1H), 6.27 (s, 1H), 4.42 (t, 2H), 4.43 (t, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.43 (unresolved, 4H), 1.95 (unresolved, 4H), 1.84 (p, 4H), 1.56 (m, 4H), 0.99 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 153.0, 150.4, 143.9, 141.5, 136.1, 127.1, 123.3, 118.6, 115.5, 111.1, 110.0, 109.8, 99.3, 68.9, 68.8, 56.9, 56.3, 50.4, 31.4, 25.2, 19.5, 19.4, 13.9. LC−MS (positive mode): m/z 483 $(M + H)^+$. Anal. Calcd for $C_{29}H_{39}NO_5$: C, 72.32; H, 8.16; N, 2.91. C, 72.27; H, 8.19; N, 3.01.

4,4′-Bis(4-(pyrrolidin-1-yl)styryl)-2,2′-bipyridine (MS 1). Under nitrogen, solid potassium *tert*-butoxide (0.45 g, 4 mmol) was added at one time to a THF solution (50 mL) of the bis-phosphonate (**2**, 0.46 g, 1 mmol) and the aldehyde (**7a**, 0.39 g, 2.2 mmol) at room temperature, and the resulting heterogeneous reaction mixture was stirred at this temperature for 3 h. The reaction mixture was subsequently quenched with water (25 mL) and evaporated to dryness, and 50 mL of methanol was added to cause precipitation of the product. It was collected by filtration, washed several times with water, methanol, and a small amount of ether, and dried in air. It was re-dissolved in dichloromethane (ca. 500 mL), and the yellow solution was concentrated to almost 20 mL. The bright yellow precipitated material was collected by filtration and dried thoroughly. The compound **MS 1** was isolated as yellow microcrystalline solid. Yield: 0.46 g (92%). Mp (differential thermal analysis, DTA): 357 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.615 (d, J = 4 Hz, 2H), 8.48 (s, 2H), 7.46 (d, J = 8 Hz, 4H), 7.41 (d, J = 16 Hz, 2H), 7.345 (d, J = 4 Hz, 2H), 6.90 (d, J = 16 Hz, 2H), 6.58 (d, J = 8 Hz, 4H), 3.35 (unresolved, 8H), 2.03 (unresolved, 8H). ^{13}C NMR was not possible because of low solubility. LC−MS (positive mode): m/z 499 $(M + H)^+$. Anal. Calcd for $C_{34}H_{34}N_4$: C, 81.89; H, 6.87; N, 11.24. Found: C, 81.72; H, 6.81; N, 11.15.

4,4′-Bis(4-dibutylamino-2,5-dimethoxystyryl)-2,2′-bipyridine (MS 2). Neat potassium *tert*-butoxide (0.45 g, 4 mmol) was added at once to a mixture of the bis-phosphonate (**2**, 0.46 g, 1 mmol) and the aldehyde (**5b**, 0.64 g, 2.2 mmol) dissolved in 50 mL of THF at room temperature under an inert atmosphere, and the dark colored reaction mixture thus obtained was stirred at this temperature for 3 h. It was then quenched with water (25 mL), and the product was extracted with dichloromethane. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and subjected to chromatographic purification over silica gel (100−200 mesh) column using methanol/chloroform 5:95 v/v as the eluent to obtain the compound **MS 2** as a dark colored thick gum. Yield: 0.66 g (90%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.635 (d, J = 4 Hz, 2H), 8.48 (s, 2H), 7.75 (d, J = 16 Hz, 2H), 7.435 (d, J = 4 Hz, 2H), 7.09 (s, 2H), 7.05 (d, J = 16 Hz, 2H), 6.50 (s, 2H), 3.88 (unresolved, 12H), 3.19 (t, 8H), 1.53−1.47 (p, 8H), 1.34−1.26 (m, 8H), 0.91 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, C-type based on DEPT-135 spectrum): δ 156.6 (C), 152.5 (C), 149.3 (CH), 147.1 (C), 146.9 (C), 142.3 (C), 128.2 (CH), 123.7 (CH), 120.3 (CH), 118.5 (CH), 117.4 (C), 111.0 (CH), 104.6 (CH), 56.3 (OMe), 52.2 (CH_2), 29.4 (CH_2), 20.5 (CH_2), 14.0 (CH_3). LC−MS (positive mode): m/z 736 $(M + H)^+$. Anal. Calcd for $C_{46}H_{62}N_4O_4$: C, 75.17; H, 8.50; N, 7.62. Found: C, 75.23; H, 8.41; N, 7.56.

4,4′-Bis(2,5-dimethoxy-4-(pyrrolidin-1-yl)styryl)-2,2′-bipyridine (MS 3). This compound was obtained using the same procedure as described for **MS 2**. Aldehyde **7b** (0.52 g, 2.2 mmol) was used instead of aldehyde **5b**. Column chromatographic purification (silica gel, 100−200 mesh) using methanol/chloroform 5:95 v/v as the mobile phase led to the isolation of the pure compound **MS 3** as a brown microcrystalline solid. Yield: 0.56 g (91%). Mp (DTA): 250 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.605 (d, J = 4 Hz, 2H), 8.46 (s, 2H), 7.75 (d, J = 16 Hz, 2H), 7.42 (d, J = 8 Hz, 2H), 7.10 (s, 2H), 6.98 (d, J = 16 Hz, 2H), 6.27 (s, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 3.44 (unresolved, 8H), 1.95 (unresolved, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, C-type based on DEPT-135 spectrum): δ 153.3 (C), 149.1 (CH), 147.4 (C), 143.8 (C), 141.8 (C), 128.4 (CH), 122.1 (CH), 120.2 (CH), 118.4 (CH), 114.4 (C), 111.4 (CH), 99.1 (CH), 56.9 (OMe), 56.2 (OMe), 50.5 (CH_2), 25.2 (CH_2). LC−MS (negative mode): m/z 618 $(M-H)^+$. Anal. Calcd. For $C_{38}H_{42}N_4O_4$: C, 73.76; H, 6.84; N, 9.05. Found: C, 73.61; H, 6.78; N, 9.15.

4,4′-Bis(4-(2,5-dimethoxy-4-dibutylaminostyryl)styryl)-2,2′-bipyridine (MS 4). Synthesis of this compound follows the same procedure as described for **MS 2**. Aldehyde **11b** (0.86 g, 2.2 mmol) was used instead of aldehyde **5b**. The crude product was purified through column chromatography using silica gel (100−200 mesh) stationary and methanol/chloroform 5:95 v/v as the mobile phases to obtain the compound **MS 4** as a thick red gum that solidified after standing at room temperature for few days. Yield: 0.87 g (93%). Mp: not measured. ^1H NMR (400 MHz, $CDCl_3$): δ 8.695 (d, J = 4 Hz, 2H), 8.56 (s, 2H), 7.59−7.53 (m, 8H), 7.50 (d, J = 16 Hz, 2H), 7.47 (d, J = 16 Hz, 2H), 7.41 (d, J = 8 Hz, 2H), 7.16−7.11 (m, 2H), 7.00 (d, J = 16 Hz, 2H), 6.55 (s, 2H), 3.88 (s, 6H,), 3.86 (s, 3H), 3.17 (t, 8H), 1.54−1.46 (p, 8H), 1.36−1.26 (m, 8H), 0.91 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, C-type based on DEPT-135 spectrum): δ 156.3 (C), 151.8 (C), 149.5 (CH), 147.5 (C), 146.0 (C), 138.9 (C), 134.8 (C), 133.2 (CH), 127.4 (CH), 126.7 (CH), 126.0 (C), 125.8 (CH), 125.3 (CH), 123.9 (CH), 121.1 (CH), 119.0 (C), 118.3 (CH), 110.3 (CH), 105.4 (CH), 56.5 (OMe), 56.3 (OMe), 52.4 (CH_2), 29.3 (CH_2), 20.5 (CH_2), 14.1 (CH_3). HRMS (MALDI−TOF/TOF, positive mode): m/z calcd. 938.571 (M^+), found 939.673 $(M + H)^+$. Anal. Calcd for $C_{62}H_{74}N_4O_4$: C, 79.28; H, 7.94; N, 5.96. Found: C, 79.35; H, 7.89; N, 5.88.

4,4′-Bis(4-(2,5-dimethoxy-4-(pyrrolidin-1-yl)styryl)styryl)-2,2′-bipyridine (MS 5). Synthesis of this compound follows the same procedure as described for **MS 1**. Aldehyde **12b** (0.74 g, 2.2 mmol) was used instead of aldehyde **7a**. The compound **MS 5** was isolated as orange microcrystalline solid. Yield: 0.72 g (87%). Mp (DTA): 274 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 8 Hz, 2H), 8.56 (s, 2H), 7.54 (s, 8H), 7.50 (d, J = 16 Hz, 2H), 7.47 (d, J = 16 Hz, 2H), 7.41 (d, J = 8 Hz, 2H), 7.16−7.11 (unresolved, 4H), 6.94 (d, J = 16 Hz, 2H), 6.31 (s, 2H), 3.88 (s, 6H), 3.86 (s, 6H), 3.41 (unresolved, 8H), 1.96 (unresolved, 8H). ^{13}C NMR was not possible because of low solubility. HRMS (MALDI−TOF/TOF, positive mode): m/z calcd. 822.415 (M^+), found 823.575 $(M + H)^+$. Anal. Calcd for $C_{54}H_{54}N_4O_4$: C, 78.80; H, 6.61; N, 6.81. Found: C, 78.96; H, 6.54; N, 6.68.

4,4′-Bis(2,5-dibutoxy-4-(4-dibutylaminostyryl)styryl)-2,2′-bipyridine (MS 6). Synthesis of this compound follows the same procedure as described for **MS 2**. Aldehyde **13b** (1.0 g, 2.2 mmol) was used instead of aldehyde **5b**. The crude product was purified by a short silica gel column (100−200 mesh) eluting with methanol/chloroform

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5:95 v/v as the mobile phase. The compound **MS 6** was isolated as a thick red gel that solidified to an orange solid after standing overnight at room temperature. Yield: 1.1 g (95%). Mp: not measured. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.675 (d, J = 4 Hz, 2H), 8.52 (s, 2H), 7.80 (d, J = 16 Hz, 2H), 7.455 (d, J = 4 Hz, 2H), 7.42 (d, J = 8 Hz, 4H), 7.28 (d, J = 16 Hz, 2H), 7.20 (d, J = 16 Hz, 2H), 7.15 (s, 2H), 7.14 (s, 2H), 7.10 (d, J = 16 Hz, 2H), 6.66 (d, J = 8 Hz, 4H), 4.11 (t, 4H), 4.07 (t, 4H), 3.31 (t, 8H), 1.93−1.87 (p, 8H), 1.66−1.57 (m, 16H), 1.41−1.36 (m, 8H), 1.08 (t, 12H), 0.99 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, C-type based on DEPT-135 spectrum): δ 156.6 (C), 151.8 (C), 150.6 (C), 149.4 (CH), 147.9 (C), 146.6 (C), 129.8 (CH), 129.4 (C), 128.4 (CH), 128.0 (CH), 125.6 (CH), 125.1 (C), 124.3 (C), 120.3 (CH), 118.9 (CH), 118.2 (CH), 111.7 (CH), 111.1 (CH), 109.8(CH), 69.2 (CH_2), 50.8 (CH_2), 31.7 (CH_2), 29.6 (CH_2), 20.4 (CH_2), 19.6 (CH_2), 14.1 (CH_3). HRMS (MALDI−TOF/TOF, positive mode): m/z calcd. 1106.759 (M^+), found 1107.748 (M + H)$^+$. Anal. Calcd for $C_{74}H_{98}N_4O_4$: C, 80.25; H, 8.92; N, 5.06. Found: C, 80.15; H, 8.78; N, 4.91.

4,4′-Bis(2,5-dibutoxy-4-(2,5-dimethoxy-4-dibutylamino-styryl)styryl)-2,2′-bipyridine (MS 7). This compound was synthesized following the same procedure as described for **MS 2**. Aldehyde **14b** (1.2 g, 2.2 mmol) was used instead of aldehyde **5b**. The crude product was purified by a short silica gel column (100−200 mesh) eluting with methanol/chloroform 5:95 v/v as the mobile phase. The compound **MS 7** was isolated as a red gum that solidified to a red solid after standing for five days at room temperature. Yield: 1.1 g (90%). Mp: not measured. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.675 (d, J = 4 Hz, 2H), 8.51 (s, 2H), 7.80 (d, J = 16 Hz, 2H), 7.51−7.46 (m, 4H), 7.37 (d, J = 16 Hz, 2H), 7.21 (d, J = 16 Hz, 2H), 7.18 (s, 2H), 7.14 (s, 4H), 6.53 (s, 2H), 4.12 (t, 4H), 4.08 (t, 4H), 3.88 (s, 6H), 3.87 (s, 6H), 3.17 (t, 8H), 1.92−1.86 (m, 8H), 1.66−1.59 (m, 8H), 1.54−1.47 (m, 8H), 1.34−1.27 (m, 8H), 1.08−1.01 (m, 12H), 0.92 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, C-type based on DEPT-135 spectrum): δ 156.5 (C), 151.8 (C), 151.7 (C), 150.8 (C), 149.3 (CH), 147.6 (C), 146.6 (C), 140.9 (C), 129.3 (C), 128.4 (CH), 125.8 (CH), 124.8 (C), 124.0 (CH), 121.1 (CH), 120.4 (CH), 119.7 (C), 118.9 (CH), 111.2 (CH), 110.5 (CH), 110.3 (CH), 105.4 (CH), 69.1 (CH_2), 56.4 (OMe), 56.2 (OMe), 52.4 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 29.4 (CH_2), 20.6 (CH_2), 19.6 (CH_2), 14.1 (CH_3). HRMS (MALDI−TOF/TOF, positive mode): m/z calcd. 1226.801 (M^+), found 1227.884 (M + H)$^+$. Anal. Calcd for $C_{78}H_{106}N_4O_8$: C, 76.31; H, 8.70; N, 4.56. Found: C, 76.25; H, 8.78; N, 4.46.

4,4′-Bis(2,5-dibutoxy-4-(2,5-dimethoxy-4-(pyrrolidin-1-yl)-styryl)styryl)-2,2′-bipyridine (MS 8). This compound was synthesized following the same procedure as described for **MS 2**. Aldehyde **15b** (1.1 g, 2.2 mmol) was used instead of aldehyde **5b**. The crude product was purified by a short silica gel column (100−200 mesh) eluting with methanol/chloroform 5:95 v/v as the mobile phase. The compound **MS 8** was isolated as a red-brown solid. Yield: 1.0 g (89%). Mp (DTA): 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.675 (d, J = 4 Hz, 2H), 8.51 (s, 2H), 7.80 (d, J = 16 Hz, 2H), 7.49 (d, J = 16 Hz, 2H), 7.45 (unresolved, 2H), 7.32 (d, J = 16 Hz, 2H), 7.22−7.14 (m, 8H), 6.32 (s, 2H), 4.12 (t, 4H), 4.07 (t, 4H), 3.88 (s, 6H), 3.85 (s, 6H), 3.42 (unresolved, 8H), 1.96 (unresolved, 8H), 1.92−1.87 (m, 8H), 1.66−1.60 (m, 8H), 1.06 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, C-type based on DEPT-135 spectrum): δ 156.6 (C), 152.5 (C), 151.8 (C), 150.7 (C), 149.4 (CH), 146.6 (C), 144.2 (C), 140.8 (C), 129.7 (C), 128.4 (CH), 125.7 (CH), 124.5 (C), 124.1 (CH), 120.3 (CH), 119.6 (CH), 118.9 (CH), 116.5 (C), 111.3 (CH), 110.8 (CH), 110.2 (CH), 99.8 (CH), 69.3 (CH_2), 69.2 (CH_2), 56.8 (OMe), 56.5 (OMe), 50.5 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 25.1 (CH_2), 19.5 (CH_2), 14.0 (CH_3). HRMS (MALDI−TOF/TOF, positive mode): m/z calcd. 1110.645 (M^+), found 1111.670 (M + H)$^+$. Anal. Calcd for $C_{70}H_{86}N_4O_8$: C, 75.64; H, 7.80; N, 5.04. Found: C, 75.49; H, 7.68; N, 5.12.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all of the new compounds, coordinates of all of the optimized geometries, tables and figures related to the computational outputs. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Lakowicz, J. R. In *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer Sciences and Business Media: New York, 2006. (b) *Springer Series on Fluorescence: Methods and Applications*; Wolfbeis, O. S., Ed.; Springer Sciences and Business Media: Berlin, Heidelberg, 2010. (c) *Topics in Fluorescence Spectroscopy*, Lakowicz, J. R., Ed.; Kluwer Academic Publishers: New York, 2002; Vols. 1−4.

(2) (a) Meier, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2482 and references therein. (b) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897 and references therein. (c) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *18*, 4619 and references therein. (d) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3 and references therein.

(3) See for example: (a) Campbell, N. H.; Smith, D. L.; Reszka, A. P.; Neidle, S.; O'Hagan, D. *Org. Biomol. Chem.* **2011**, *9*, 1328. (b) Janovec, L.; Kožurková, M.; Sabolová, D.; Ungvarský, J.; Paulíková, H.; Plšíková, J.; Vantová, Z.; Imrich, J. *Bioorg. Med. Chem.* **2011**, *19*, 1790. (c) Sparapani, S.; Haider, S. M.; Doria, F.; Gunaratnam, M.; Neidle, S. *J. Am. Chem. Soc.* **2010**, *132*, 12263. (d) Würdemann, M.; Christoffers, J. *Org. Biomol. Chem.* **2010**, *8*, 1894. (e) Rogness, D. C.; Larock, R. C. *J. Org. Chem.* **2010**, *75*, 2289.

(4) See for example: (a) Egawa, T.; Koide, Y.; Hanaoka, K.; Komatsu, T.; Terai, T.; Nagano, T. *Chem. Commun.* **2011**, 4162. (b) Li, T.; Yang, Z.; Li, Y.; Liu, Z.; Qi, G.; Wang, B. *Dyes Pigm.* **2011**, *88*, 103. (c) Shi, W.; Sun, Z.; Wei, M.; Evans, D. G.; Duan, X. *J. Phys. Chem. C* **2010**, *114*, 21070. (d) McQueen, P. D.; Sagoo, S.; Yao, H.; Jockusch, R. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 9193. (e) Santra, M.; Ko, S.-K.; Shin, I.; Ahn, K. H. *Chem. Commun.* **2010**, *46*, 3964.

(5) See for example: (a) Zanotti, K. J.; Silva, G. L.; Creeger, Y.; Robertson, K. L.; Waggoner, A. S.; Berget, P. B.; Armitage, B. A. *Org. Biomol. Chem.* **2011**, *9*, 1012. (b) Fischer, G. M.; Daltrozzo, E.; Zumbusch, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1406. (c) Yuan, L.; Lin, W.; Song, J. *Chem. Commun.* **2010**, *46*, 7930. (d) Samanta, A.; Vendrell, M.; Das, R.; Chang, Y.-T. *Chem. Commun.* **2010**, *46*, 7406.

(e) Pandey, A. K.; Deakin, P. C.; Jansen-Van Vuuren, R. D.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2010**, *22*, 3954.

(6) See for example: (a) Bag, B.; Pal, A. *Org. Biomol. Chem.* **2011**, *9*, 4467. (b) Wang, C.; Wong, K. M.-C. *Inorg. Chem.* **2011**, *50*, 5333. (c) Beija, M.; Afonso, C. A. M.; Martinho, J. M. G. *Chem. Soc. Rev.* **2009**, *38*, 2410. (d) Kim, H. N.; Lee, M. H.; Kim, H. J.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2008**, *37*, 1465. (e) Koide, Y.; Urano, Y.; Hanaoka, K.; Terai, T.; Nagano, T. *J. Am. Chem. Soc.* **2011**, *133*, 5680.

(7) See for example: (a) Wu, W.; Wu, W.; Ji, S.; Guo, H.; Zhao, J. *Dalton Trans.* **2011**, *40*, 5953. (b) Semeniuchenko, V.; Groth, U.; Khilya, V. *Synthesis* **2009**, 3533. (c) Jana, R.; Partridge, J. J.; Tunge, J. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 5157. (d) Shiraishi, Y.; Sumiya, S.; Hirai, T. *Chem. Commun.* **2011**, *47*, 4953. (e) Dong, Y.; Li, J.; Jiang, X.; Song, F.; Cheng, Y.; Zhu, C. *Org. Lett.* **2011**, *13*, 2252.

(8) See for example: (a) Nepomnyashchii, A. B.; Bröring, M.; Ahrens, J.; Bard, A. J. *J. Am. Chem. Soc.* **2011**, *133*, 8633. (b) Chase, D. T.; Young, B. S.; Haley, M. M. *J. Org. Chem.* **2011**, *76*, 4043. (c) Chase, D. T.; Young, B. S.; Haley, M. M. *Inorg. Chem.* **2011**, *50*, 4392. (d) Khan, T. K.; Rao, M. R.; Ravikanth, M. *Eur. J. Org. Chem.* **2010**, 2314. (e) Rao, M. R.; Mobin, S. M.; Ravikanth, M. *Tetrahedron* **2010**, *66*, 1728.

(9) See for example: (a) Arun, K. T.; Jayaram, D. T.; Avirah, R. R.; Ramaiah, D. *J. Phys. Chem. B* **2011**, *115*, 7122. (b) Jisha, V. S.; Arun, K. T.; Hariharan, M.; Ramaiah, D. *J. Phys. Chem. B* **2010**, *114*, 5912. (c) Sreejith, S.; Divya, K. P.; Ajayaghosh, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 7883. (d) Sreejith, S.; Carol, P.; Chithra, P.; Ajayaghosh, A. *J. Mater. Chem.* **2008**, *18*, 264. (e) Ajayaghosh, A. *Acc. Chem. Res.* **2005**, *38*, 449.

(10) See for example: (a) Vijayakumar, C.; Praveen, V. K.; Kartha, K. K.; Ajayaghosh, A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4942. (b) Dasgupta, D.; Srinivasan, S.; Rochas, C.; Thierry, A.; Schröder, A.; Ajayaghosh, A.; Guenet, J. M. *Soft Mater.* **2011**, *7*, 2797. (c) Babu, S. S.; Kartha, K. K.; Ajayaghosh, A. *J. Phys. Chem. Lett.* **2010**, *1*, 3413. (d) Prasanthkumar, S.; Gopal, A.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2010**, *132*, 13206. (e) Mahesh, S.; Thirumalai, R.; Yagai, S.; Kitamura, A.; Ajayaghosh, A. *Chem. Commun.* **2009**, 5984.

(11) See for representative examples: (a) Hu, B.; Fu, S.-J.; Xu, F.; Tao, T.; Zhu, H. -Y.; Cao, K.-S.; Huang, W.; You, X.-Z. *J. Org. Chem.* **2011**, *76*, 4444. (b) Lee, H.-S.; Kim, H.-J.; Kang, J.-G. *Photochem. Photobiol. Sci.* **2011**, *10*, 1338. (c) Peng, X.; Wu, T.; Fan, J.; Wang, J.; Zhang, S.; Song, F.; Sun, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 4180. (d) Cao, X.; Lin, W.; Ding, Y. *Chem.—Eur. J* **2011**, *17*, 9066. (e) Yuasa, J.; Mitsui, A.; Kawai, T. *Chem. Commun.* **2011**, *47*, 5807. (f) Ulrich, G.; Goeb, S.; Nicola, A. D.; Retailleau, P.; Ziessel, R. *J. Org. Chem.* **2011**, *76*, 4489. (g) Mahmood, T.; Paul, A.; Ladame, S. *J. Org. Chem.* **2010**, *75*, 204. (h) Bürckstümmer, H.; Weissenstein, A.; Bialas, D.; Würthner, F. *J. Org. Chem.* **2011**, *76*, 2426. (i) Chen, Y.; Wang, H.; Wan, L.; Bian, Y.; Jiang, J. *J. Org. Chem.* **2011**, *76*, 3774.

(12) For example, see: (a) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553. (b) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892. (c) Smith, A. P.; Fraser, C. L. *Comprehensive Coordination Chemistry II*; Elsevier: New York, 2003; Vol. 1, pp 1−23.

(13) (a) Maury, O.; Le Bozec, H. *Acc. Chem. Res.* **2005**, *38*, 691 and references therein. (b) Bouder, T. L.; Viau, L.; Guégan, J.-P.; Maury, O.; Le Bozec, H. *Eur. J. Org. Chem.* **2002**, 3024. (c) Aubert, V.; Ishow, E.; Ibersiene, F.; Boucekkine, A.; Williams, J. A. G.; Toupet, L.; Métivier, R.; Nakatani, K.; Guerchais, V.; Le Bozec, H. *New J. Chem.* **2009**, *33*, 1320. (d) Maury, O.; Guégan, J.-P.; Renouard, T.; Hilton, A.; Dupau, P.; Sandon, N.; Toupet, L.; Le Bozec, H. *New J. Chem.* **2001**, *25*, 1553. (e) Araya, J. C.; Gajardo, J.; Moya, S. A.; Aguirre, P.; Toupet, L.; Williams, J. A. G.; Escadeillas, M.; Le Bozec, H.; Guerchais, V. *New J. Chem.* **2010**, *34*, 21. (f) Bourgault, M.; Renouard, T.; Lognoné, B.; Mountassir, C.; Le Bozec, H. *Can. J. Chem.* **1997**, *75*, 318. (g) Lohio, O.; Viau, L.; Maury, O.; Le Bozec, H. *Tetrahedron Lett.* **2007**, *48*, 1229. (h) Viau, L.; Maury, O.; Le Bozec, H. *Tetrahedron Lett.* **2004**, *45*, 125.

(14) (a) Kocian, O.; Mortimer, R. J.; Beer, P. D. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3203. (b) Abdel-Shafi, A. A.; Beer, P. D.; Mortimer, R. J.; Wilkinson, F. *J. Phys. Chem. A* **2000**, *104*, 192. (c) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Dalton Trans.* **1993**, 2629. (d) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 333. (e) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *Analyst* **1992**, *117*, 1247. (f) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1460. (g) Abbotto, A.; Bellotto, L.; Angelis, F.; De; Manfredi, N.; Marinzi, C. *Eur. J. Org. Chem.* **2008**, 5047. (h) An, B.-K.; Burn, P. L.; Meredith, P. *Chem. Mater.* **2009**, *21*, 3315. (i) Grabulosa, A.; Martineau, D.; Beley, M.; Gros, P. C.; Cazzanti, S.; Caramori, S.; Bignozzi, C. A. *Dalton Trans.* **2009**, 63.

(15) (a) Berner, D.; Klein, C.; Nazeeruddin, M. K.; Angelis, F. D.; Castellani, M.; Scopelliti, P. B. R.; Zuppirolid, L.; Grätzel, M. *J. Mater. Chem.* **2006**, *16*, 4468. (b) Klein, C.; Baranoff, E.; Nazeeruddin, Md. K.; Grätzel, M. *Tetrahedron Lett.* **2010**, *51*, 6161.

(16) (a) Sreejith, S.; Divya, K. P.; Ajayaghosh, A. *Chem. Commun.* **2008**, 2903. (b) Ajayaghosh, A.; Carol, P.; Sreejith, S. *J. Am. Chem. Soc.* **2005**, *127*, 14962. (c) Divya, K. P.; Sreejith, S.; Balakrishna, B.; Jayamurthy, P.; Aneesa, P.; Ajayaghosh, A. *Chem. Commun.* **2010**, *46*, 6069.

(17) (a) Le Bozec, H.; Renouard, T. *Eur. J. Inorg. Chem.* **2000**, 229. (b) Sénéchal, K.; Maury, O.; Le Bozec, H.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **2002**, *124*, 4560. (c) Maury, O.; Viau, L.; Sénéchal, K.; Corre, B.; Guégan, J.-P.; Renouard, T.; Ledoux, I.; Zyss, J.; Le Bozec, H. *Chem.—Eur. J.* **2004**, *10*, 4454. (d) Aubert, V.; Guerchais, V.; Ishow, E.; Hoang-Thi, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 577. (e) Coe, B. J.; Fielden, J.; Foxon, S. P.; Brunschwig, B. S.; Asselberghs, I.; Clays, K.; Samoc, A.; Samoc, M. *J. Am. Chem. Soc.* **2010**, *132*, 3496.

(18) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Campbell, W. M.; Burrell, A. K.; Officer, D. L.; Jolley, K. W. *Coord. Chem. Rev.* **2004**, *248*, 1363. (c) Shao, W.; Gu, F.; Gai, L.; Li, C. *Chem. Commun.* **2011**, *47*, 5046. (d) Monari, A.; Assfeld, X.; Beley, M.; Gros, P. C. *J. Phys. Chem. A* **2011**, *115*, 3596. (e) Jennings, J. R.; Liu, Y.; Wang, Q.; Zakeeruddin, S. M.; Grätzel, M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6637. (f) Koster, L. J. A.; Kemerink, M.; Wienk, M. M.; Maturová, K.; Janssen, R. A. J. *Adv. Mater.* **2011**, *23*, 1670. (g) Lee, C.-H.; Chiu, W.-H.; Lee, K.-M.; Hsieh, W.-F.; Wu, J.-M. *J. Mater. Chem.* **2011**, *21*, 5114. (h) Fabregat-Santiago, F.; Bisquert, J.; Cevey, L.; Chen, P.; Wang, M.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2009**, *131*, 558. (i) Listorti, A.; O'Regan, B.; Durrant, J. R. *Chem. Mater.* **2011**, *23*, 3381. (j) Clifford, J. N.; Martínez-Ferrero, E.; Viterisi, A.; Palomares, E. *Chem. Soc. Rev.* **2011**, *40*, 1635. (k) Vougioukalakis, G. C.; Philippopoulos, A. I.; Stergiopoulos, T.; Falaras, P. *Coord. Chem. Rev.* **2011**, *255*, 2602. (l) Reynal, A.; Palomares, E. *Eur. J. Inorg. Chem.* **2011**, 4509.

(19) (a) Chatterjee, T.; Sarma, M.; Das, S. K. *Tetrahedron Lett.* **2010**, *51*, 1985. (b) Chatterjee, T.; Sarma, M.; Das, S. K. *Tetrahedron Lett.* **2010**, *51*, 6906. (c) Chatterjee, T.; Sarma, M.; Das, S. K. *Tetrahedron Lett.* **2011**, *52*, 5460.

(20) (a) Smith, A. P.; Lamba, J. J. S.; Fraser, C. L. *Org. Synth.* **2004**, *10*, 107. (b) Fraser, C. L.; Anastasi, N. R.; Lamba, J. J. S. *J. Org. Chem.* **1997**, *62*, 9314.

(21) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319−2358.

(22) (a) Parker, C. A. In *Measurement of Fluorescence Efficiency*; Elsevier Publishing Co.: New York, 1968. (b) Kartens, T.; Kobs, K. *J. Phys. Chem.* **1980**, *84*, 1871.

(23) Rurack, K.; Spieles, M. *Anal. Chem.* **2011**, *83*, 1232.

(24) Frisch, M. J. et al. *Gaussian09, revision B.01*; Gaussian, Inc.: Wallingford, CT, 2010.

(25) Toro, C.; Boni, L. D.; Yao, S.; Belfield, K. D.; Hernández, F. E. *J. Phys. Chem. B* **2008**, *112*, 12185.

(26) Dreuw, A.; Head-Gordon, M. *J. Am. Chem. Soc.* **2004**, *126*, 4007 and references therein.

(27) Yanai, T.; Tew, D.; Handy, N. *Chem. Phys. Lett.* **2004**, *393*, 51.