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Chromophores Arranged as “Magnetic Meta Atoms”: Building Blocks for Molecular Metamaterials

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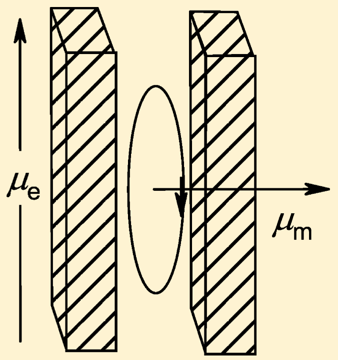
Ⓢ *Supporting Information*

ABSTRACT: Benzoperylenetriscarboximides were parallel arranged by stiff spacers where exciton interactions could be controlled by their distance. The most bathochromic electronic transition of the chromophores essentially exhibits only an electric component where an orthogonal magnetic component was established by the distance-controlled interaction of chromophores. Such arrangements were discussed as building blocks for molecular metamaterials.



INTRODUCTION

Metamaterials[1] are attracting more interest in science and technology because special interactions with electromagnetic waves can be expected. Such materials were created for microwave radiation and allowed the generation of devices with unusual properties, such as negative indices of refraction[2] where applications for camouflage[3] are the most prominent. Unusual optical properties can be expected from the creation of metamaterials in the visible spectrum.

The orthogonal arrangement of the electric and magnetic components of the interaction with electromagnetic radiation is typical for metamaterials. This was realized for microwaves with a periodically ordered framework of specially formed electric conductors formally forming “magnetic meta atoms”. U-shaped conductors were applied where two vertical lines of the U form electrical dipoles and the interlinking bow of the U a pathway for the generation of an orthogonal magnetic component; see Figure 1, left. A strong coupling between coplanar oriented linear *anti*-operating oscillators[4] would be an alternative where the orthogonal magnetic component is induced by the dielectric displacement current; see Figure 1, right.

We tried to reduce the size of such components down to the molecular scale by the exchange of the electric conductors with conjugated π-systems where electrons are as mobile as in metallic wires.[5] The resonances of the metallic oscillators become equivalent to the eigenvalues of the π-systems. The transversal coupling according to Figure 1, right, corresponds to a H arrangement of chromophores[6] (compare exciton coupling and Scheibe’s H-aggregates[7]). Suitable chromophores and spacers are required as building blocks for such complex structures.

We used benzoperylenetriscarboximides[8] **1** as resonating components because there is only one very pure electronic π–π* transition in the visible region polarized along the molecular long axis (Chart 1).[9] As a consequence, the electric component of light absorption dominates and parasitic magnetic components become unimportant. We targeted to introduce magnetic components by exciton interactions in multichromophores composed of parallel arranged **1**.

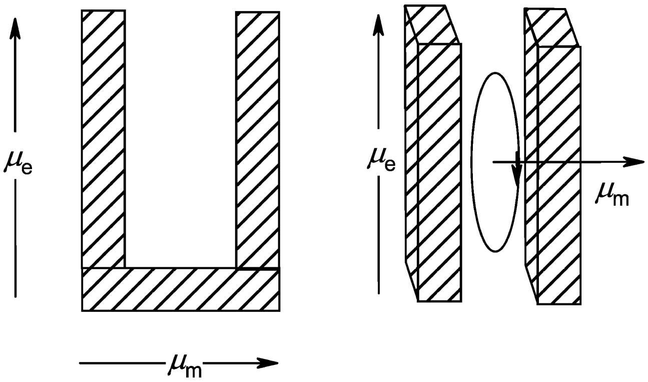


Figure 1. Left: U-shaped conductor for metamaterials. μ_e = electrical dipole; μ_m = orthogonal magnetic dipole. Right: Transversal coupling of two conductors and dielectric displacement current inducing a magnetic moment for metamaterials.

RESULTS AND DISCUSSION

The solubility of complex multichromophores with basic structures of **1** is expected to be very low and interferes with UV/vis spectroscopic investigations. As a consequence, the solubility-increasing 1-hexylheptyl substituent[10] was attached to

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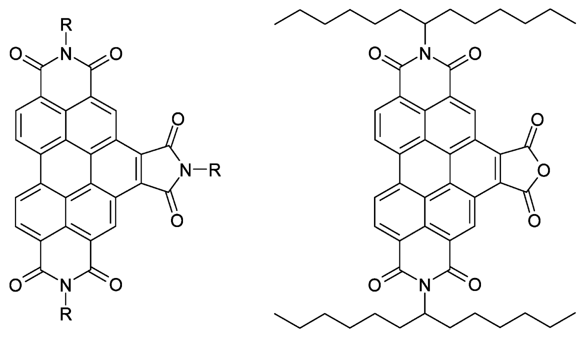
Chart 1. Benzoperylenetriscarboximides 1 and Anhydride 2 as Building Blocks for Synthesis



the nitrogen atoms of the six-membered ring carboximides where the five-membered ring carboximide was used for the interlinking between chromophores. The anhydride[8] **2** was a good starting material for synthesis where **1** can be obtained by the condensation with primary amines.

First, naphthalenetetracarboxylic anhydride (**3**) was condensed with hydrazine to form *N,N*′-diaminonaphthalenecarboximide[11] (**4**) as a reactive spacer and further condensed with **2** to give the trichromophore **5** with parallel units of **1** caused by steric effects of the carbonyl groups; see Scheme 1. Analogously, 1,4-diamino-2,3,5,6-tetramethylbenzene was allowed to react with[12] **3** and further with **2** to form the trichromophore **7** with a longer spacer with extra stiffness by steric effects of the methyl groups. Perylenetetracarboxylic bisanhydride (**8**) was similarly condensed with hydrazine for the preparation[13,14] of **9** with a long, bathochromically absorbing aromatic spacer, and finally condensed with 1,4-diamino-2,3,5,6-tetramethylbenzene to obtain the arrangement **12** with a very long spacer. Material **14** with a flexible spacer was obtained in a similar way. As an alternative, the anhydride **2** was condensed with hydrazine and diaminotetramethylbenzene to form the amino derivatives **15** and **16**, respectively (Chart 2). A further condensation with naphthalene-1,8:4,5-tetracarboxylic bisanhydride (**3**) and perylene-3,4:9,10-tetracarboxylic bisanhydride (**8**) gave the corresponding trichromophores in similar yields; however, preparation procedures and purification proved to be more laborious.

Chiral derivatives of **1** were prepared in order to investigate the importance of magnetic components for the electronic transitions; compare ref 15. **2** was condensed with an excess of diaminodimethylbiphenyl[16] to prepare the monochromophore **17** with an axially chiral biphenyl at the periphery. The condensation of the diamine with an excess of the anhydride allowed the preparation of the chiral dyad **18** (Chart 3).

Scheme 1. Synthesis of the Arrangements 5, 7, 10, 12, and 14 (R = 1-Hexylheptyl): (i) $N_2H_4{\cdot}H_2O$, Imidazole; (ii) Quinoline

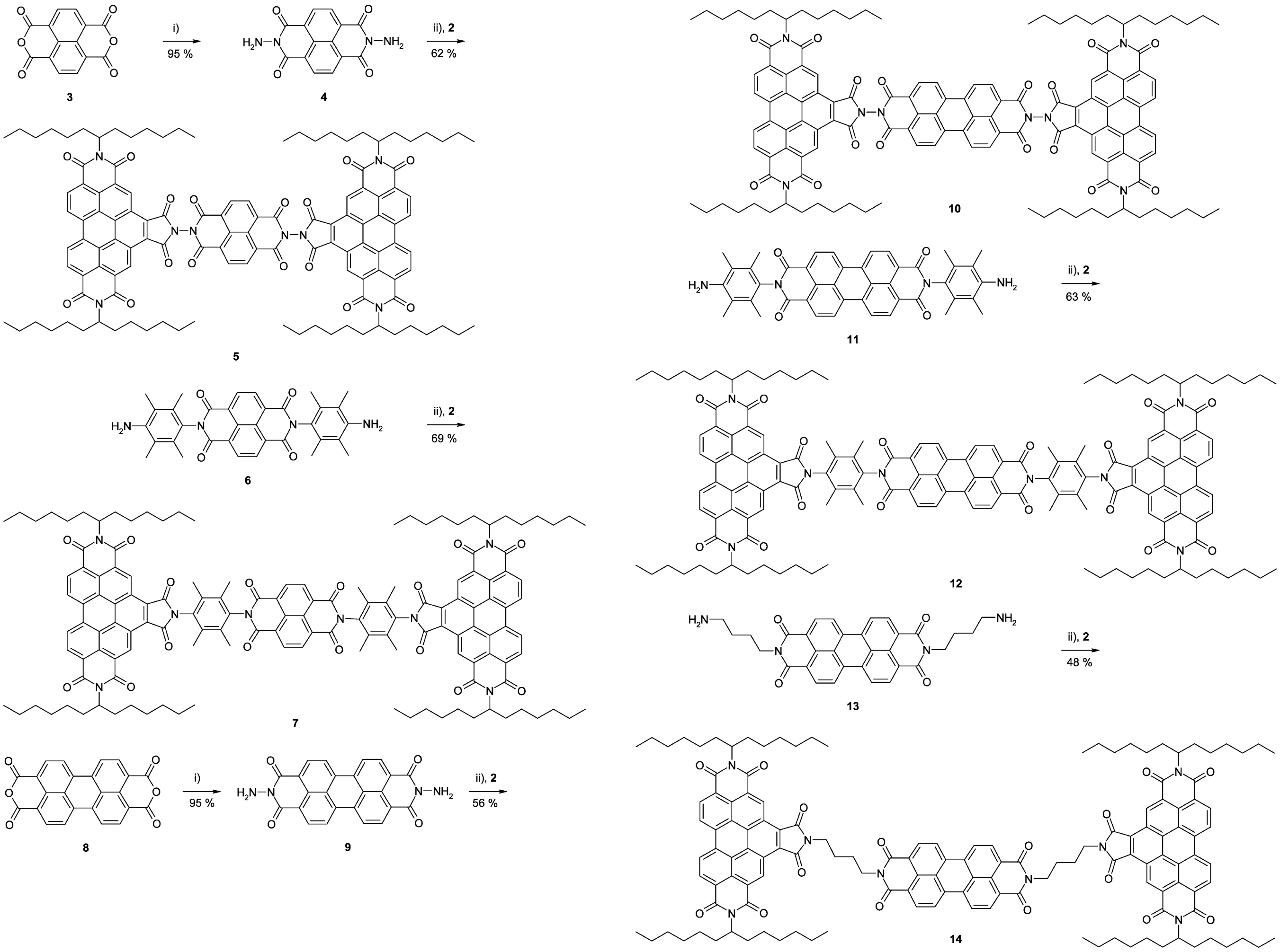
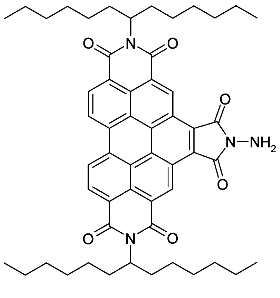


Chart 2. Amino Intermediates 15 and 16



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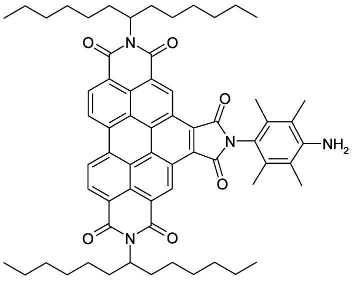

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The UV/vis absorption of **1** is strongly structured with a maximum of about 470 nm where fluorescence is mirror-type; see Figure 2, dashed line. The UV/vis spectra of the chiral dye **17** were examined for an estimation of electric (μ_e) and parasitic magnetic (μ_m) components of the electronic transition in the visible range.[17] The absorption and fluorescence spectra of **17** were essentially identical with the spectra of **1**; see dashed lines in the inset in Figure 3. The CD spectrum of **17** represents the baseline of the spectrometer and is an indication that there is no significant parasitic magnetic component in the electronic transition. As a consequence, the electronic transition in the visible region is a very pure $\pi-\pi^*$ type with μ_e. Thus, no interfering magnetic component of the electronic transition can be expected. We tested the introduction of magnetic components (μ_m) into the transition by means of exciton interactions in the dyad **18** by the sandwich-like chiral arrangement. The thus-induced magnetic component μ_m is indicated by the strong CD effects with $\Delta\varepsilon$ of about −250, where the negative CD effect is consistent with a (*P*) geometry of **18**; see Figure 3, solid line. The dihedral angle of the biphenyl with regard to the nitrogen atoms in **18** is less than 90°, and the electric transition moment is parallel to the long axis of the chromophore. The bonds to the five-ring nitrogen atoms of the chromophores are orthogonal to the transition moments. As a consequence, the angle between the transition moments is more than 90° and is thus verified by the observed negative CD effect.

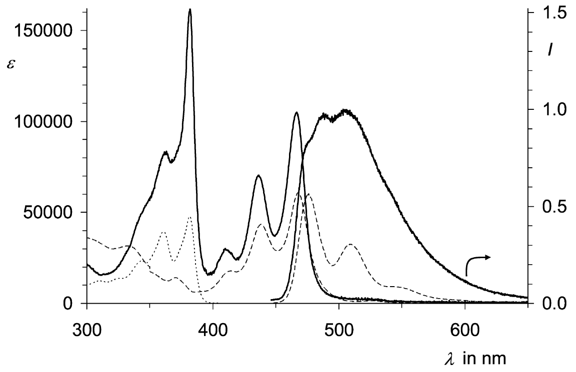


Figure 2. UV/vis absorption and fluorescence spectra in chloroform. Dashed absorption (left) and fluorescence (right) spectra of **1**. Dotted lines: Absorption spectrum of *N,N′*-bis-1-methylpropylnaphthalene-1,8:4,5-tetracarboxylic bisimide. Solid lines: Absorption (left) and fluorescence (right) spectra of **5** (spacer 1).

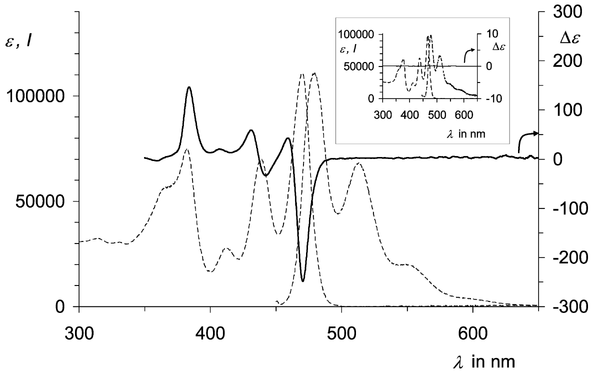
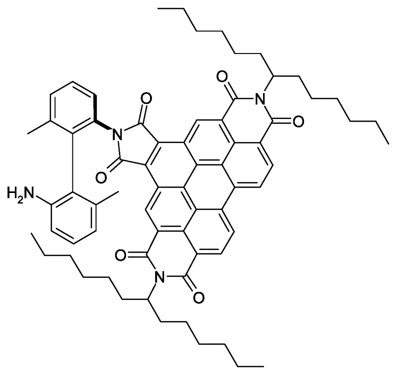


Figure 3. UV/vis absorption (dashed on the left) and fluorescence spectra (dashed on the right) of **18** and the CD spectrum (solid line) in chloroform. Inset: Spectra of **17**; the CD spectrum is essentially the baseline.

Two parallel electric transition moments μ_e according to Figure 1 are realized by the stiff arrangement of benzoperylene chromophores **1** to form a H-type geometry in **5** with a distance of about 22 Å (spacer 1). Exciton interactions cause a perpendicular magnetic component μ_m; the consequences of such interactions can be seen in the absorption spectrum in

Chart 3. Chiral benzoperylenetriscarboximide 17 and Chiral Dyad 18



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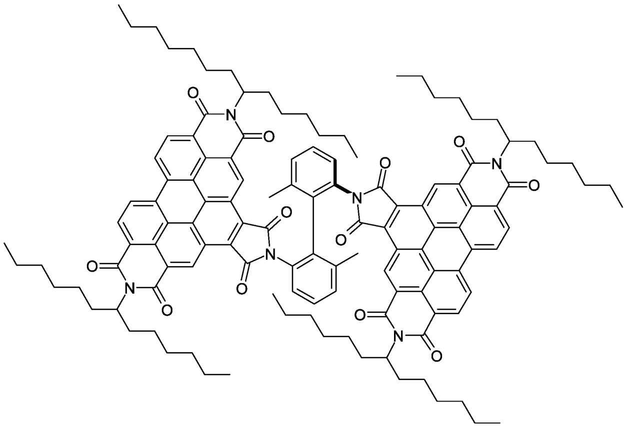

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Figure 2 (solid line). The most bathochromic absorption of **5** (>400 nm) is more intense than that in **1**; however, it does not reach twice the intensity as would be expected from a simple additive effect of the individual chromophores. Thus, the exciton interaction is destructive to the efficiency of light absorption. The individual bands are slightly hypsochromically shifted, and the bandwidth is diminished. On the other hand, an extraordinarily sharp absorption at 380 nm into a higher excited state becomes dominant, partially overlaid by the naphthalene biscarboximide; sharp resonances are typical for metamaterials (see ref 18). Parallel oriented perylenecarboximides in substituted xanthenes in positions 4 and 5 were previously reported;[19] however, there was no sharp hypsochromic absorptions; the spectra resemble more of a skew-type arrangement of chromophores.[19] On the other hand, the intensity of the sharp absorption of **5**, ε = 162 000, exceeds the sum of the absorption of the involved chromophores by far (dotted and dashed lines in Figure 2). The high ε value may be partially caused by the unusually low half-width of the line where the integral represents the intensity of the transition. The geometry of **5** corresponds to a perfect H arrangement of the chromophores of **1** and should not exhibit fluorescence according to Förster's concept. On the other hand, a broad bathochromically shifted fluorescence band with a quantum yield of 0.2 is observed. We interpret these results as a consequence of a relaxation of the excited state to intramolecular excimers with skew transition moments; compare ref 20.

The longer still stiff spacer in **7** separates the transition moments to 30 Å. As a consequence, exciton interactions become weaker and the UV/vis spectrum is more close to an addition of the spectra of the involved chromophores (Figure 4). There is only a slight effect of diminishing the most bathochromic absorption. The sharp intense absorption at 380 nm still exists as the most intense absorption, but it exceeds only slightly the band at 465 nm.

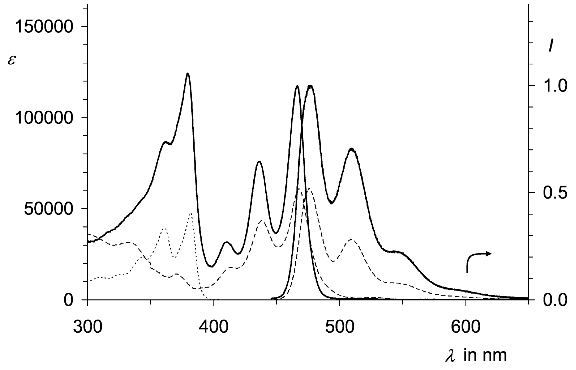


Figure 4. UV/vis absorption and fluorescence spectra in chloroform. Solid lines: Absorption (left) and fluorescence (right) spectra of **7** (spacer 2). Dashed lines: Absorption (left) and fluorescence (right) spectra of **1**. Dotted lines: Absorption spectrum of *N,N*′-bis-1-methylpropylnaphthalene-1,8:4,5-tetracarboxylic bisimide.

The perylenetetracarboxbismide in **10** forms a slightly shorter spacer of 26 Å compared with the latter (spacer 3). The absorption at 465 nm is still slightly diminished with respect to the sum of the components (Figure 5). The apparent absorption at 377 nm is much less pronounced than that for **5** and **7**; however, it is essentially caused by exciton interactions because light absorption is weak for all chromophoric components of **10** in this spectral region. The fluorescence of the chromophore **1** in **10** is completely quenched, and efficient energy transfer to the more bathochromically absorbing central perylenebiscarboximide unit is observed as indicated by a fluorescence quantum yield close to unity of the latter if the former is excited at 436 nm. This is remarkable because electric transition moments are orthogonal and the energy transfer forbidden by Förster's theory; compare ref 21.

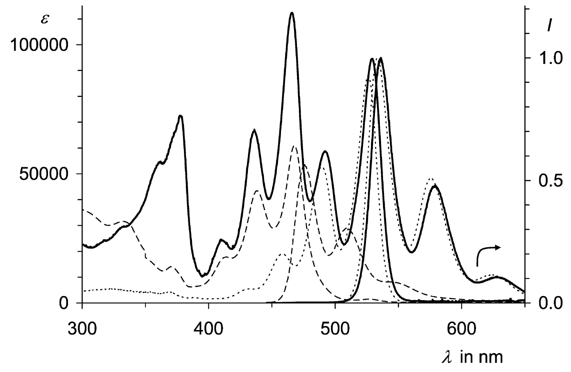


Figure 5. UV/vis absorption and fluorescence spectra in chloroform. Solid lines: Absorption (left) and fluorescence (right) spectra of **10** (spacer 3). Dashed lines: Absorption (left) and fluorescence (right) spectra of **1**. Dotted lines: Absorption and fluorescence spectra of *N,N*′-bis-1-hexylheptylperylene-3,4:9,10-tetracarboxylic bisimide.

The introduction of further tetramethylphenylene spacers in **12** (spacer 4) separates the two chromophores of **1** by 34 Å (distance of the N−N connection lines of the six-membered ring carboximides). Exciton interactions become weaker because of the large distance; however, they are still present as can be seen at the band at 375 nm (Figure 6). Energy transfer proceeds as efficiently as in **10** so that a quantum efficiency of close to unity is obtained.

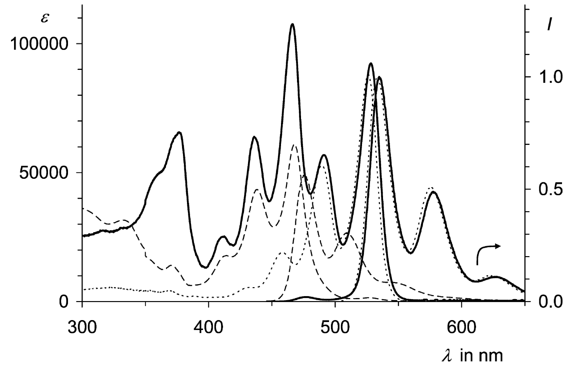


Figure 6. UV/vis absorption and fluorescence spectra in chloroform. Solid lines: Absorption (left) and fluorescence (right) spectra of **12** (spacer 4). Dashed lines: Absorption (left) and fluorescence (right) spectra of **1**. Dotted lines: Absorption and fluorescence spectra of *N,N*′-bis-1-hexylheptylperylene-3,4:9,10-tetracarboxylic bisimide.

The introduction of the long, flexible spacer in **14** changes the spectroscopic behavior fundamentally (spacer 5). The exciton-induced band at 374 nm is still present; however, the absorptivities are generally appreciably lowered (Figure 7). The absorption at 464 nm of two chromophores is even lower than that of a single chromophore, and similarly, the absorptivity of the centrally linking perylenecarboximide is remarkably low, where only 1/4 of the absorptivity of isolated chromophores is

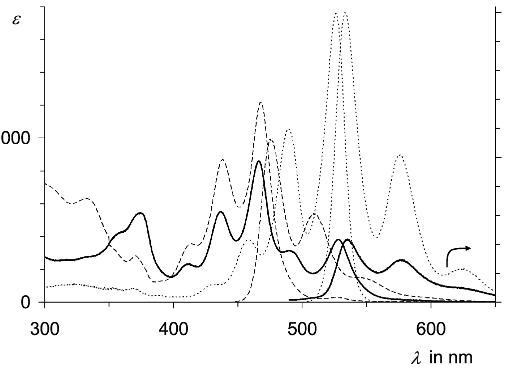


Figure 7. UV/vis absorption and fluorescence spectra in chloroform. Solid lines: Absorption (left) and fluorescence (right) spectra of **14** (spacer 5). Dashed lines: Absorption (left) and fluorescence (right) spectra of **1**. Dotted lines: Absorption and fluorescence spectra of *N*,*N*′-bis-1-hexylheptylperylene-3,4:9,10-tetracarboxylic bisimide.

reached. Both line type and absorptivity remain unchanged if the solution of **14** is diluted. We interpret this result as a consequence of internal aggregation-like interaction of the involved chromophores. The second hypsochromic vibronic band of the central unit is as well amplified as the mirror-type fluorescent band. Such effects and diminished absorptivity are typical for H-type aggregation of chromophores. Moreover, the fluorescence quantum yield of 75% is still high, however, it is appreciably lower than for **7** or **10**; this is a further indicator for H-type arrangements of chromophores.

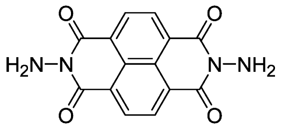
Finally, multichromophoric systems with orthogonal electric and magnetic transition moments such as **5**, **7**, **10**, and **12** have to be regularly arranged in space to obtain macroscopic optical metamaterials. This may be successful by the application of liquid crystals.

■ CONCLUSIONS

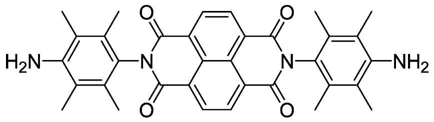
Molecular components for metamaterials in the visible region can be constructed by a stiff arrangement of parallel oriented chromophores with dominating $\pi-\pi^*$ transitions. Exciton interactions introduce orthogonal magnetic components controlled by the intramolecular distance; the smallest spacer in H-shaped arrangements given in compound **5** seems to be the most promising candidate for metamaterials. Flexible spacers cause a more complex behavior where intramolecular aggregation-like interaction is observed. A combination of various chromophores allows intramolecular energy transfer processes, although the electronic transition moments are orthogonally arranged.

■ EXPERIMENTAL SECTION

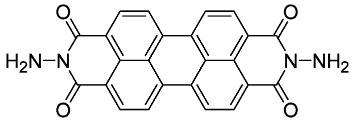
General. All FAB spectra were recorded in 3-nitrobenzylalcohol as the matrix.



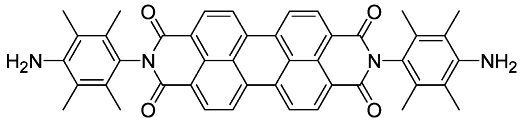
*2,7-Diaminobenzo[lmn][3,8]phenanthrolin-1,3,6,8-tetraone (**4**, Spacer 1).* Isochromeno[6,5,4-*def*]isochromen-1,3,6,8-tetraone (**3**, 500 mg, 1.87 mmol) was dissolved in melt imidazole (5 g), treated with hydrazine hydrate (234 mg, 4.68 mmol), stirred at 100 °C for 17 h, allowed to cool, precipitated with 2 M aqueous HCl (300 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, and dried at 110 °C for 16 h: Yield 526 mg (95%) ochre solid, mp >300 °C; R_f (silica gel, chloroform) 0.00; MS (DEP/EI) *m*/*z* (%) 297.2 (15) [M^+ + H], 296.2 (100) [M^+], 294.2 (11), 281.2 (24), 267.2 (47), 266.2 (14), 252.2 (16), 238.2 (15), 181.1 (11).



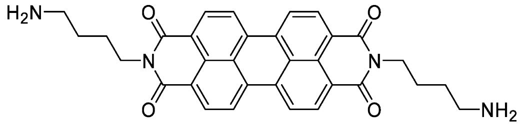
*2,7-Bis-(4-amino-2,3,5,6-tetramethylphenyl)benzo[lmn][3,8]-phenanthrolin-1,3,6,8-tetraone (**6**, Spacer 2).* Isochromeno[6,5,4-*def*]isochromen-1,3,6,8-tetraone (**3**, 2.00 g, 7.46 mmol) was dissolved in melt imidazole (10 g), treated with 2,3,5,6-tetramethylbenzene-1,4-diamine (3.06 g, 18.6 mmol), stirred at 110 °C for 17 h, allowed to cool, precipitated with 2 M aqueous HCl (500 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, and dried at 110 °C for 16 h: Yield 4.2 g (98%) ochre solid, mp >300 °C; MS (MALDI, anthracene) *m*/*z*: 560.4 [M^+].



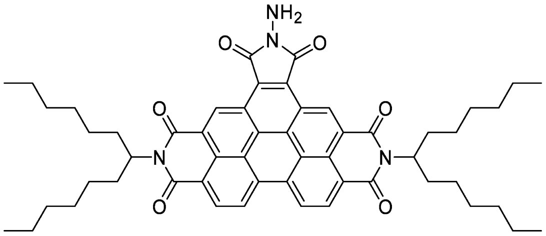
*2,9-Diaminoanthra[2,1,9-def;6,5,10-d′e′f′]diisoquinolin-1,3,8,10-tetraone (**9**, Spacer 3).* Perylene-3,4:9,10-tetracarboxylic bisanhydride (**8**, 1.00 g, 2.55 mmol) and imidazole (5 g) were heated at 100 °C, treated with hydrazine hydrate (417 mg, 0.013 mmol), stirred at 100 °C for 5 h, allowed to cool, precipitated with 2 M aqueous HCl (300 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, and dried at 110 °C for 16 h: Yield 1.05 g (95%) red solid, mp >300 °C; IR (ATR: $\tilde{\nu}$ = 3258.6 (w), 1733.0 (w), 1699.7 (vs), 1662.2 (s), 1633.2 (w), 1593.8 (s), 1575.8 (m), 1558.2 (m), 1505.5 (w), 1456.3 (w), 1436.3 (w), 1417.1 (w), 1401.4 (m), 1368.2 (m), 1253.9 (m), 1174.3 (m), 1123.7 (w), 976.4 (w), 959.2 (w), 901.6 (w), 805.7 (vs), 798.0 (w), 791.7 (w), 747.9 (w), 733.5 (vs), 663.7 cm^{-1} (w); MS (DEP/EI) *m*/*z* (%) 420.1 (12) [M^+], 97.1 (12), 83.1 (12), 69.1 (27), 67.1 (11), 57.1 (19), 56.1 (12), 55.1 (20), 44.0 (100), 43.0 (24), 41.0 (26); HRMS (FAB^+, quadrupole, $C_{24}H_{12}N_4O_4$) calcd *m*/*z* 420.0859, found *m*/*z* 420.0863, Δ = −0.0004.



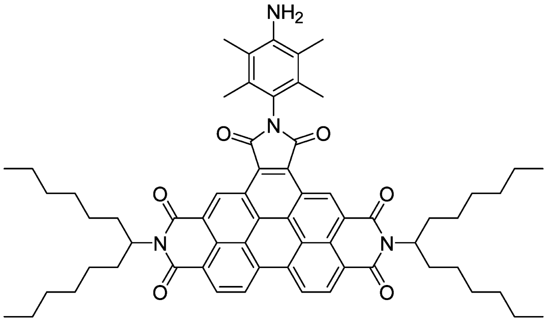
*2,9-Bis-(4-amino-2,3,5,6-tetramethylphenyl)anthra[2,1,9-def;6,5,10-d′e′f′]diisoquinolin-1,3,8,10-tetraone (**11**, Spacer 4).* Perylene-3,4:9,10-tetracarboxylic bisanhydride (**8**, 1.00 g, 2.55 mmol) in imidazole (10 g) was heated at 140 °C, treated with 2,3,5,6-tetramethylbenzene-1,4-diamine (2.10 g, 12.8 mmol), stirred at 140 °C for 4 h, allowed to cool, precipitated with 2 M aqueous HCl (300 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, and dried at 110 °C for 16 h: Yield 1.66 g (95%) red solid, mp >300 °C; R_f (silica gel, chloroform/ethanol 20:1) 0.36; UV/vis ($CHCl_3$) λ_{max} (E_{rel}) = 461.4 (0.23), 489.8 (0.61), 526.6 nm (1.00); fluorescence ($CHCl_3$, λ_{exc} = 490 nm) λ_{max} (I_{rel}) = 531.8 (1.00), 574.6.0 nm (0.55); fluorescence quantum yield ($CHCl_3$, λ_{exc} = 490 nm, $E_{490nm/1cm}$ = 0.0992, reference S-13 with Φ = 1.00) 0.10; MS (DEP/EI) *m*/*z* (%) 686.3 (11) [M^+ + 2H] 685.3 (21) [M^+ + H], 684.3 (62) [M^+], 149.1 (40), 148.1 (40), 147.1 (100), 134.1 (42), 132.1 (15), 105.1 (12), 91.1 (21), 77.0 (12), 55.1 (10), 44.0 (56), 41.1 (13); HRMS (FAB^+, quadrupole, $C_{44}H_{36}N_4O_4$) calcd *m*/*z* 684.2737, found *m*/*z* 684.2737, Δ = ± 0.0000.



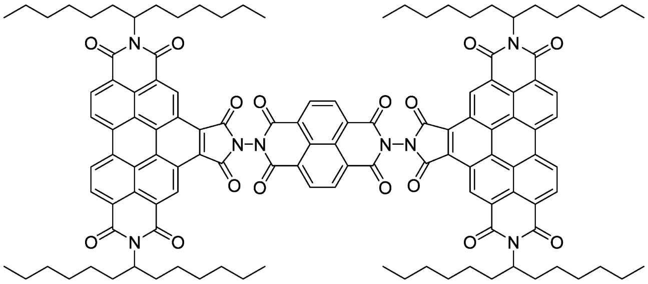
*2,9-Bis-(4-aminobutyl)anthra[2,1,9-def;6,5,10-d′e′f′]diisoquinolin-1,3,8,10-tetraone (**13**, Spacer 5).* Perylene-3,4:9,10-tetracarboxylic bisanhydride (**8**, 1.00 g, 2.55 mmol) was heated with imidazole (10 g) at 140 °C, treated with butan-1,4-diamine (1.13 g, 12.8 mmol), stirred at 140 °C for 4 h, allowed to cool, precipitated with 2 M aqueous HCl (300 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, and dried at 110 °C for 16 h: Yield 1.20 g (95%) red solid, mp >250 °C; MS (MALDI, anthracene) m/z 533.6 [M^+ + H].



N,N′′-Bis(1-hexylheptyl)-N′-(amino)benzo[ghi]perylene-2,3,8,9,11,12-hexacarboxylic-2,3,8,9-bis(dicarboximide)-11,12-imide (15). Method 1: 2,10-Bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno-[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 300 mg, 0.360 mmol) and hydrazine hydrate (88.6 mg, 1.77 mmol) in imidazole (2.5 g) were stirred at 120 °C for 4 h, allowed to cool, precipitated with 2 M aqueous HCl (40 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, dried at 110 °C for 16 h, and purified by column separation (silica gel 40−63 μm, toluene): Yield 87.0 mg (28%) yellow solid. *Method 2*: 2,10-Bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 100 mg, 0.118 mmol), hydrazinium sulfate (67.8 mg, 0.590 mmol), and imidazole (1.0 g) were stirred at 140 °C for 4 h, allowed to cool, precipitated with 2 M aqueous HCl (20 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, dried at 110 °C for 16 h, and purified by column separation (silica gel 40−63 μm, toluene): Yield 79.4 mg (78%) yellow solid. *Method 3*: 2,10-Bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 100 mg, 0.118 mmol), hydrazinium chloride (37.1 mg, 0.353 mmol), and imidazole (1.6 g) were stirred at 140 °C for 12 h, allowed to cool, precipitated with 2 M aqueous HCl (20 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl and distilled water, dried at 110 °C for 16 h, and purified by column separation (silica gel 40−63 μm, toluene): Yield 76.4 mg (75%) yellow solid, mp >250 °C; R_f (silica gel, $CHCl_3$/ethanol 5:1) 0.74; IR (ATR) $\tilde{\nu}$ = 3509.7 (w), 3396.2 (w), 3138.8 (w), 3114.8 (w), 2953.1 (w), 2921.9 (m), 2853.3 (m), 2630.9 (w), 1748.8 (w), 1699.5 (m), 1651.1 (vs), 1595.8 (m), 1576.0 (m), 1499.7 (w), 1456.5 (w), 1440.8 (w), 1404.0 (w), 1363.0 (m), 1349.7 (s), 1321.7 (m), 1270.3 (w), 1252.0 (m), 1177.7 (w), 1145.4 (w), 1119.4 (w), 1050.8 (w), 938.3 (w), 901.7 (w), 842.2 (w), 812.9 (s), 802.9 (w), 761.8 (w), 749.6 (m), 723.1 cm^{-1} (w); UV/vis ($CHCl_3$) λ_{max} (E_{rel}) = 344 (0.66), 359 (0.73), 433 (0.42), 457 (0.86), 489 nm (1.00); fluorescence ($CHCl_3$, λ_{exc} = 460 nm) λ_{max} (I_{rel}) = 478 (0.61), 499 (1.00), 533 nm (0.71); fluorescence quantum yield ($CHCl_3$, λ_{exc} = 460 nm, $E_{460nm/1cm}$ = 0.0267, reference S-13 with Φ = 1.00) 0.04; MS (DEP/EI) m/z (%) 863 (21) [M^+ + H], 862 (34) [M^+], 722 (14), 682 (29), 681 (71), 680 (41), 666 (18), 500 (43), 499 (97), 498 (100), 484 (17), 483 (14), 85 (27), 83 (61), 70 (15), 69 (35), 67 (18), 57 (29), 56 (14), 55 (36), 44 (98), 43 (21), 41 (65); HRMS (FAB$^+$, quadrupole, $C_{54}H_{62}N_4O_6$) calcd m/z 862.4669, found m/z 862.4663, Δ = −0.0006. Anal. Calcd for $C_{54}H_{62}N_4O_6$ (862.5): C, 75.15; H, 7.24; N, 6.49. Found: C, 74.83; H, 7.37; N, 6.58.

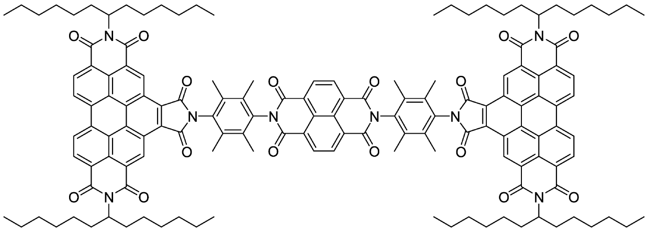


*N,N′′-Bis(1-hexylheptyl)-N′-(4-amino-2,3,5,6-tetramethylphenyl)-benzo[ghi]perylene-2,3,8,9,11,12-hexacarboxylic-2,3,8,9-bis-(dicarboximide)-11,12-dicarboximide (**16**).* 2,10-Bis(1-hexylheptyl)-furo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 300 mg, 0.353 mmol) and 2,3,5,6-tetramethylbenzene-1,4-diamine (290 mg, 1.77 mmol) in quinoline were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (40 mL), and extracted three times with chloroform. The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40−63 μm, toluene): Yield 446 mg (76%) brownish yellow solid, mp >250 °C; R_f (silica gel, $CHCl_3$/ethanol 5:1) 0.93; IR (ATR) $\tilde{\nu}$ = 3407.8 (w), 2956.3 (w), 2924.8 (w), 2856.9 (w), 1983.4 (w), 1772.7 (w), 1712.9 (s), 1662.3 (s), 1625.5 (m), 1595.2 (w), 1521.8 (w), 1563.8 (w), 1521.8 (w), 1457.7 (w), 1414.6 (m), 1394.6 (w), 1363.8 (m), 1317.2 (vs), 1275.1 (w), 1250.0 (w), 1233.4 (w), 1201,1 (w), 1174.9 (w), 1113.4 (w), 946.2 (w), 873.2 (w), 843.9 (w), 811.3 (m), 766.0 (w), 746.0 (w), 724.9 (w), 660.2 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS) δ = 0.81 (t, ^3J(H,H) = 6.9 Hz, 12 H, 4 × CH_3), 1.06−1.65 (m, 32 H, 16 × CH_2), 1.85−2.04 (m, 4 H, 2 × β-CH_2), 2.14−2.44 (m, 16 H, 2 × β-CH_2, 12 × CH_3), 5.20−5.36 (m, 2 H, 2 × NCH), 9.06−9.53 (m, 4 H, 4 × $CH_{perylene}$), 10.51 ppm (s, 2 H, 2 × $CH_{perylene}$); ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS) δ = 14.0, 15.7, 15.9, 22.6, 27.0, 29.2, 31.8, 32.4, 55.3, 123.5, 123.8, 124.1, 125.0, 125.2, 126.9, 127.3, 127.4, 127.7, 128.3, 130.4, 133.0, 133.4, 133.8 ppm; MS (DEP/EI) m/z (%) 996 (77) [M^+ + H], 995 (100) [M^+], 814 (18), 813 (34), 812 (21), 657 (10), 632 (12), 631 (23), 630 (26), 149 (20), 148 (59), 147 (25), 134 (14), 97 (11), 83 (19), 70 (15), 69 (38), 57 (14), 56 (18), 55 (51), 43 (21), 41 (24); HRMS (FAB$^+$, quadrupole, $C_{64}H_{74}N_4O_6$) calcd m/z 994.5608, found m/z 994.5595, Δ = −0.0013. Anal. Calcd for $C_{64}H_{74}N_4O_6$ (994.6): C, 77.23; H, 7.49; N, 5.63. Found: C, 77.44; H, 7.47; N, 5.47.

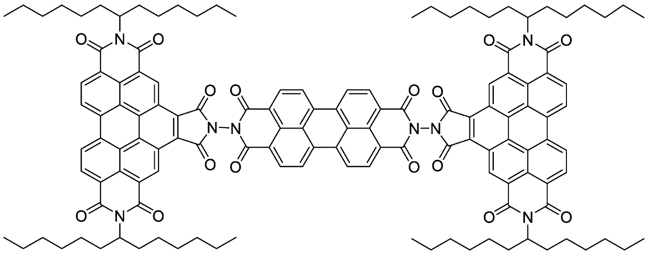


*Dye **5** (Spacer 1).* 2,7-Diaminobenzo[*lmn*][3,8]phenanthrolin-1,3,6,8-tetraone (**4**, 83.0 mg, 0.280 mmol) and 2,10-bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 500 mg, 0.588 mmol) in quinoline (8 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (40 mL), and extracted three times with chloroform (3 × 80 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40−63 μm, toluene): Yield 340 mg (62%) yellow solid, mp >300 °C; R_f (silica gel, chloroform/ethanol 40:1) 0.60; IR (ATR) $\tilde{\nu}$ = 2948.4 (w), 2923.4 (m), 2854.9 (w), 1794.2 (w), 1739.1 (m), 1704.0 (s), 1661.7 (vs), 1624.9 (w), 1595.4 (w), 1583.7 (w), 1558.1 (w), 1538.5 (w), 1520.5 (w), 1456.0 (w), 1412.7 (w), 1393.3 (w), 1363.3 (m), 1337.8 (w), 1306.5 (vs), 1274.4 (w), 1240.1 (m), 1212.0 (w), 1199.1 (w), 1183.2 (w), 1172.1 (m), 1123.7 (w), 1099.1 (w), 1020.7

(w), 981.3 (w), 937.3 (w), 879.4 (w), 866.0 (w), 849.0 (w), 829.0 (w), 812.5 (s), 778.4 (w), 764.2 (m), 748.0 (m), 726.4 (w), 657.7 cm^{-1} (w); ^{1}H NMR (600 MHz, CDCl$_3$, 27 °C, TMS) δ = 0.82 (t, 24 H, ^3J(H,H) = 7.1 Hz, 8 × CH$_3$), 1.20–1.48 (m, 64 H, 16 × CH$_2$), 1.91–2.00 (m, 8 H, 4 × β-CH$_2$), 2.30–2.40 (m, 8 H, 4 × β-CH$_2$), 5.26–5.35 (m, 4 H, 4 × NCH), 9.06–9.10 (m, 4 H, 4 × $\mathrm{CH_{perylene}}$), 9.20–9.30 (m, 4 H, 4 × $\mathrm{CH_{naphthalene}}$), 9.50 (d, 4 H, ^3J(H,H) = 8.5 Hz 4 × $\mathrm{CH_{perylene}}$), 10.43–10.46 ppm (m, 4 H, 4 × $\mathrm{CH_{perylene}}$); ^{13}C NMR (150 MHz, CDCl$_3$, 27 °C, TMS) δ = 14.0, 22.6, 27.0, 29.2, 31.7, 55.4, 123.4, 124.4, 125.3, 125.9, 127.0, 127.7, 127.9, 128.6, 132.6, 133.5 159.8, 163.5 ppm; UV/vis (CHCl$_3$) λ_{max} (ε) = 362.8 (66600), 382.3 (124400), 410.2 (30100), 436.5 (73000), 466.5 nm (105000); fluorescence (CHCl$_3$, λ_{exc} = 436 nm) λ_{max} (I_{rel}) = 489.4 (0.99), 505.1 nm (1.00); fluorescence quantum yield (CHCl$_3$, λ_{exc} = 436 nm, $E_{436nm/1cm}$ = 0.0075, reference S-13 with Φ = 1.00) 0.19; MS (FAB$^+$) m/z (%) 1958.8 (10) [M$^+$ + 2H], 1957.7 (1) [M$^+$ + H], 1956.8 [M$^+$], 1230.1 (25), 1230.1 (25). Anal. Calcd for $C_{122}H_{124}N_8O_{16}$ (1956.9): C, 74.82; H, 6.38; N, 5.72. Found: C, 74.51; H, 6.47; N, 5.72.

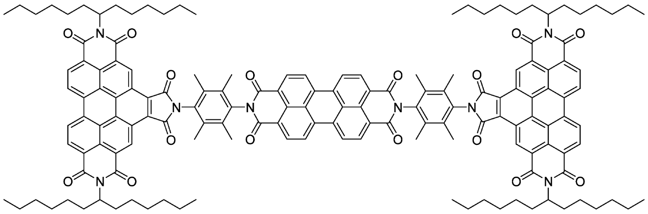


Dye **7** *(Spacer 2).* 2,7-Bis-(4-amino-2,3,5,6-tetramethylphenyl)-benzo[*lmn*][3,8]phenanthrolin-1,3,6,8-tetraone (**6**, 105 mg, 0.187 mmol) and 2,10-bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 350 mg, 0.411 mmol) in quinoline (8 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (40 mL), and extracted three times with chloroform (3 × 80 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene): Yield 276 mg (69%) yellow solid, mp >300 °C; R_f (silica gel, chloroform/ethanol 40:1) 0.65; IR (ATR) $\tilde{\nu}$ = 2948.0 (w), 2923.2 (m), 2855.0 (w), 1794.7 (w), 1739.0 (m), 1704.0 (s), 1661.9 (vs), 1624.5 (w), 1595.2 (w), 1583.7 (w), 1557.9 (w), 1538.1 (w), 1520.0 (w), 1456.5 (w), 1412.7 (w), 1393.0 (w), 1363.2 (m), 1337.7 (w), 1306.0 (vs), 1274.2 (w), 1240.5 (m), 1211.8 (w), 1199.0 (w), 1183.2 (w), 1172.1 (m), 1123.7 (w), 1099.1 (w), 1020.7 (w), 981.3 (w), 937.0 (w), 879.4 (w), 866.5 (w), 849.5 (w), 829.0 (w), 812.5 (s), 778.4 (w), 764.2 (m), 748.3 (m), 657.5 cm^{-1} (w); ^{1}H NMR (600 MHz, CDCl$_3$, 27 °C, TMS) δ = 0.82 (t, 24 H, ^3J(H,H) = 7.1 Hz, 8 × CH$_3$), 1.20–1.48 (m, 64 H, 16 × CH$_2$), 1.91–2.00 (m, 8 H, 4 × β-CH$_2$), 2.22 (s, 12 H, 4 × CH$_3$), 2.32 (s, 12 H, 4 × CH$_3$), 2.29–2.40 (m, 8 H, 4 × β-CH$_2$), 5.26–5.35 (m, 4 H, 4 × NCH), 9.06–9.10 (m, 4 H, 4 × $\mathrm{CH_{naphthalene}}$), 9.20–9.30 (m, 4 H, 4 × $\mathrm{CH_{perylene}}$), 9.50 (d, 4 H, ^3J(H,H) = 8.5 Hz, 4 × $\mathrm{CH_{perylene}}$), 10.43–10.46 ppm (m, 4 H, 4 × $\mathrm{CH_{perylene}}$); ^{13}C NMR (150 MHz, CDCl$_3$, 27 °C, TMS) δ = 14.0, 15.4, 16.0, 22.6, 27.0, 29.2, 31.8, 32.4 55.3, 123.6, 124.2, 125.3, 127.0, 127.5, 127.8, 128.4, 131.8, 132.8, 134.4, 162.2, 167.0 ppm; UV/vis (CHCl$_3$) λ_{max} (E_{rel}) = 362.2 (0.69), 379.4 (1.00), 410.4 (0.24), 436.5 (0.61), 466.4 nm (0.94); fluorescence (CHCl$_3$, λ_{exc} = 436 nm) λ_{max} (I_{rel}) = 475.8 (1.00), 508.1 nm (0.70); fluorescence quantum yield (CHCl$_3$, λ_{exc} = 436 nm, $E_{436nm/1cm}$ = 0.0135, reference S-13 with Φ = 1.00) 0.27; MS (FAB$^+$) m/z (%) 2220.2 (10) [M$^+$ − H].



Dye **10** *(Spacer 3). Method 1:* 2,10-Bis(1-hexylheptyl)furo-[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11-(2*H*,10*H*)-hexone (**2**, 200 mg, 0.236 mmol) and 2,9-diaminoanthra-[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-1,3,8,10-tetraone (**9**, 40.0 mg, 0.094 mmol) in quinoline (5 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (20 mL), and extracted three times with chloroform (3 × 50 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene): Yield 110 mg (56%) orange solid.

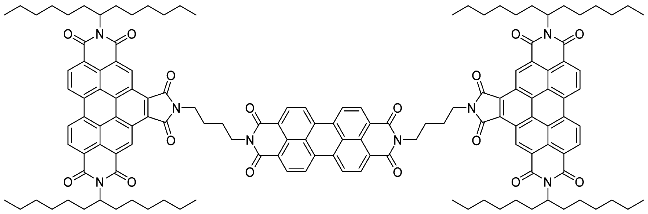
Method 2: Perylene-3,4:9,10-tetracarboxylicbisanhydride (**8**, 100 mg, 0.255 mmol) and **15** (551 mg, 0.638 mmol) in quinoline (3 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (15 mL), and extracted three times with chloroform (3 × 50 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene): Yield 345 mg (65%) orange solid, mp >300 °C; R_f (silica gel, chloroform/ethanol 40:1) 0.65; IR (ATR) $\tilde{\nu}$ = 2923.1 (m), 2854.1 (m), 2360.0 (m), 2338.0 (m), 1974.5 (w), 1950.0 (w), 1936.8 (w), 1913.6 (w), 1903.3 (w), 1875.1 (w), 1862.6 (w), 1839.4 (w), 1819.9 (w), 1796.4 (w), 1778.0 (w), 1765.4 (w), 1744.6 (m), 1726.7 (m), 1704.2 (s), 1698.0 (m), 1692.5 (m), 1659.4 (vs), 1649.9 (w), 1642.0 (w), 1629.2 (w), 1612.0 (w), 1592.0 (s), 1573.3 (w), 1565.3 (w), 1548.5 (w), 1535.8 (w), 1529.8 (w), 1513.1 (w), 1493.7 (w), 1483.5 (w), 1467.8 (w), 1462.0 (w), 1451.9 (w), 1443.3 (w), 1432.7 (w), 1422.2 (w), 1413.2 (m), 1402.3 (m), 1391.8 (w), 1365.6 (m), 1345.4 (w), 1309.9 (vs), 1241.5 (m), 1211.0 (m), 1170.3 (m), 1126.3 (m), 968.1 (w), 954.0 (w), 939.5 (w), 903.0 (w), 877.9 (w), 849.1 (w), 808.1 (m), 776.4 (w), 762.1 (w), 748.0 (w), 734.0 (m), 698.4 (w), 672.1 (w), 658.0 cm^{-1} (w); ^{1}H NMR (400 MHz, CDCl$_3$, 27 °C, TMS) δ = 0.82 (t, 24 H, ^3J(H,H) = 6.7 Hz, 8 × CH$_3$), 1.19–1.68 (m, 64 H, 16 × CH$_2$), 1.92–2.05 (m, 8 H, β-CH$_2$), 2.28–2.44 (m, 8 H, β-CH$_2$), 5.25–5.37 (m, 4 H, NCH), 8.25–8.72 (m, 8 H, 8 × $\mathrm{CH_{perylene}}$), 9.18–9.58 (m, 8 H, 8 × $\mathrm{CH_{perylene}}$), 10.32–10.46 ppm (m, 4 H, 4 × $\mathrm{CH_{perylene}}$); ^{13}C NMR (100 MHz, CDCl$_3$, 27 °C, TMS) δ = 14.0, 22.6, 27.0, 29.3, 29.7, 31.8, 32.4, 55.4, 122.7, 123.2, 123.5, 124.6, 125.1, 125.9, 127.7, 128.3, 129.4, 132.6, 133.4, 134.9 160.1, 163.7 ppm; UV/vis (CHCl$_3$) λ_{max} (ε) = 378.6 (83700), 410.9 (30900), 436.5 (80300), 466.5 (130300), 492.1 (70400), 528.9 nm (112400); fluorescence (CHCl$_3$, λ_{exc} = 436 nm) λ_{max} (I_{rel}) = 536.3 (1.00), 579.1 (0.48), 627.0 nm (0.11); fluorescence quantum yield (CHCl$_3$, λ_{exc} = 436 nm, $E_{436nm/1cm}$ = 0.0088, reference C25 with Φ = 1.00) 1.00. Anal. Calcd for $C_{132}H_{128}N_8O_{16}$ (2080.9): C, 76.13; H, 6.20; N, 5.38. Found: C, 75.96; H, 6.31; N, 5.24.



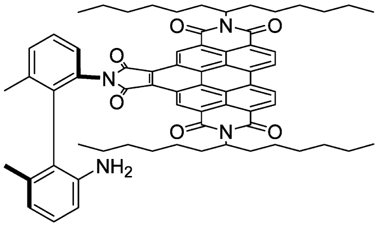
Dye **12** *(Spacer 4). Method 1:* 2,10-Bis(1-hexylheptyl)furo-[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11-(2*H*,10*H*)-hexone (**2**, 1.00 g, 1.18 mmol) and 2,9-bis-(4-amino-2,3,5,6-tetramethylphenyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**11**, 384 mg, 0.561 mmol) in quinoline (5 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (20 mL), and extracted three times with chloroform (3 × 50 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene): Yield 830 mg (63%) orange solid.

Method 2: Perylene-3,4:9,10-tetracarboxylicbisanhydride (**7**, 100 mg, 0.255 mmol) and **16** (635 mg, 0.638 mmol) in quinoline (3 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (15 mL), and extracted three times with chloroform (3 × 50 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene): Yield 419 mg (63%) orange solid, mp >300 °C; R_f

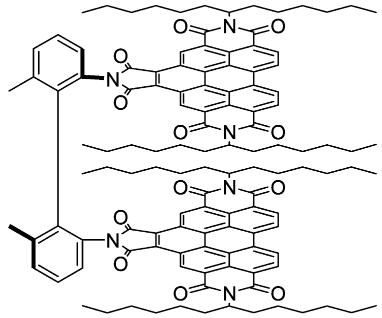
(silica gel, chloroform/ethanol 20:1) 0.80; IR (ATR) $\tilde{\nu}$ = 2924.8 (m), 2855.3 (m), 2362.0 (m), 2337.0 (m), 1983.3 (w), 1949.8 (w), 1929.0 (w), 1900.3 (w), 1875.1 (w), 1853.3 (w), 1834.6 (w), 1819.9 (w), 1806.2 (w), 1797.0 (w), 1787.7 (w), 1777.6 (w), 1765.7 (w), 1754.5 (w), 1744.4 (w), 1738.2 (w), 1722.1 (m), 1709.8 (s), 1691.8 (w), 1678.7 (w), 1665.5 (vs), 1659.5 (vs), 1649.8 (w), 1641.6 (w), 1630.8 (w), 1620.4 (w), 1611.8 (w), 1594.0 (s), 1572.9 (w), 1565.1 (w), 1548.4 (w), 1529.9 (w), 1513.1 (w), 1501.8 (w), 1493.7 (w), 1480.4 (w), 1432.3 (w), 1426.4 (w), 1413.5 (w), 1365.9 (m), 1344.3 (s), 1334.6 (s), 1317.7 (vs), 1274.0 (w), 1233.0 (w), 1250.1 (w), 1233.0 (w), 1200.4 (w), 1174.2 (w), 1118.6 (w), 1017.4 (w), 957.9 (w), 851.9 (w), 811.8 (m), 767.6 (w), 748.2 (w), 724.2 (w), 662.7 cm^{-1} (w); ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS) δ = 0.82 (t, 24 H, ^3J(H,H) = 6.8 Hz, 8 × CH_3), 1.18–1.65 (m, 64 H, 16 × CH_2), 1.89–2.01 (m, 8 H, β-CH_2), 2.22 (s, 12 H, 4 × CH_3), 2.30 (s, 12 H, 4 × CH_3), 2.28–2.43 (m, 8 H, β-CH_2), 5.24–5.39 (m, 4 H, NCH), 8.76–8.95 (m, 8 H, 8 × $CH_{perylene}$), 9.10–9.30 (m, 4 H, 4 × $CH_{perylene}$), 9.41–9.54 (m, 4 H, 4 × $CH_{perylene}$), 10.30–10.45 ppm (m, 4 H, 4 × $CH_{perylene}$); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS) δ = 14.0, 15.5, 15.9, 22.6, 27.0, 29.2, 29.7, 31.8, 32.4, 55.3, 123.5, 123.6, 124.2, 125.3, 126.9, 127.5, 127.8, 128.4, 130.3, 132.2, 132.9, 133.5, 134.2, 135.2, 162.8, 167.1 ppm; UV/vis ($CHCl_3$) λ_{max} (ε) = 376.3 (80600), 410.9 (33500), 436.5 (81400), 466.5 (133400), 491.4 (66400), 528.2 nm (107600); fluorescence ($CHCl_3$, λ_{exc} = 436 nm) λ_{max} (I_{rel}) = 535.8 (1.00), 579.4 (0.49), 626.5 nm (0.11); fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436nm/1cm}$ = 0.0045, reference C25 with Φ = 1.00) 1.00. Anal. Calcd for $C_{152}H_{152}N_8O_{16}$ (2345.1): C, 77.79; H, 6.39; N, 4.77. Found: C, 77.61; H, 6.46; N, 4.64.



Dye 14 (Spacer 5). 2,10-Bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno-[2,1,10-*def*:7,8,9-*d*′*e*′*f*′]diisoquinoline-1,3,5,7,9,11(2*H*,10H)-hexone (**2**, 350 mg, 0.413 mmol) and 2,9-bis(4-aminobutyl)anthra[2,1,9-*def*;6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,8,10-tetraone (**13**, 100 mg, 0.188 mmol) in quinoline (8 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (20 mL), and extracted three times with chloroform (3 × 50 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene): Yield 198 mg (48%) dark red solid, mp >300 °C; R_f (silica gel, chloroform/ethanol 20:1) 0.25; IR (ATR) $\tilde{\nu}$ = 2952.7 (m), 2924.6 (s), 2855.5 (m), 1768.6 (w), 1700.4 (vs), 1659.2 (vs), 1625.4 (m), 1593.9 (s), 1578.0 (w), 1559.6 (w), 1540.2 (w), 1522.2 (w), 1506.8 (w), 1456.7 (w), 1438.0 (w), 1400.2 (m), 1363.3 (m) 1343.4 (m), 1316.2 (s), 1272.2 (m), 1239.2 (m), 1204.0 (w), 1173.1 (w), 1125.5 (w), 1125.5 (w), 1101.2 (w), 973.8 (w), 943.4 (w), 846.5 (w), 810.1 (m), 795.1 (w), 765.7 (w), 744.9 (w), 659.1 (w), 626.0 (w), 616.6 cm^{-1} (w); UV/vis ($CHCl_3$) λ_{max} (ε) = 374.1 (61000), 410.9 (26900), 436.5 (64000), 466.5 (98900), 489.8 (36600), 528.2 nm (43000); fluorescence ($CHCl_3$, λ_{exc} = 436 nm) λ_{max} (I_{rel}) = 535.4 (1.00), 576.0 nm (0.68); fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436nm/1cm}$ = 0.0219, reference C25 with Φ = 1.00) 0. 75. Anal. Calcd for $C_{140}H_{144}N_8O_{16}$ (2193.1): C, 76.62; H, 6.61; N, 5.11. Found: C, 76.53; H, 6.72; N, 5.17.



Dye 17. 2,10-Bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d*′*e*′*f*′]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 401 mg, 0.472 mmol) and (*P*)(+) 6,6′-dimethylbiphenyl-2,2′-diamine (100 mg, 0.472 mmol) in quinoline (1.5 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (20 mL), and extracted three times with chloroform (3 × 80 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene, second band): Yield 930 mg (20%) yellow solid, mp >300 °C; R_f (silica gel, chloroform/ethanol 40:1) 0.81; IR (ATR) $\tilde{\nu}$ = 3377.4 (w), 2953.9 (m), 2923.6 (vs), 2855.1 (s), 2362.1 (w), 2337.3 (w), 1774.8 (w), 1716.4 (s), 1702.2 (s), 1660.6 (vs), 1625.9 (m), 1594.4 (m), 1524.3 (w), 1463.5 (m), 1413.8 (m), 1364.4 (s), 1317.3 (s), 1276.4 (m), 1242.6 (m), 1209.8 (w), 1174.1 (w), 1163.7 (w), 1121.2 (w), 971.5 (w), 941.8 (w), 850.5 (w), 812.1 (m), 766.2 (m), 747.6 (w), 659.4 cm^{-1} (w); ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS) δ = 0.72–0.86 (m, 12 H, 4 × CH_3), 0.87–1.43 (m, 32 H, 32 × CH_3), 1.87–1.98 (m, 4 H, 2 × β-CH_2), 2.16 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.31–2.38 (m, 4 H, 2 × β-CH_2), 5.28–5.32 (m, 2 H, NCH), 6.85–7.00 (m, 2 H, 2 × $CH_{aromat.}$), 7.40–7.80 (m, 4 H, 4 × $CH_{aromat.}$), 9.10–9.26 (m, 2 H, 2 × $CH_{perylene}$), 9.30–9.45 (m, 2 H, 2 × $CH_{perylene}$), 10.33–10.48 ppm (m, 2 H, 2 × $CH_{perylene}$); ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS) δ = 14.0, 19.9, 22.6, 27.0, 29.1, 29.2, 31.7, 32.5, 55.3, 124.1, 125.1, 127.7, 128.5 ppm; UV/vis ($CHCl_3$) λ_{max} (ε) = 377.5 (37400), 410.9 (15600), 436.8 (39400), 467.3 nm (60900); fluorescence ($CHCl_3$, λ_{exc} = 437 nm) λ_{max} (I_{rel}) = 478.7 (1.00), 511.9 (0.69), 548.8 nm (0.18); fluorescence quantum yield ($CHCl_3$, λ_{exc} = 437 nm, $E_{437nm/1cm}$ = 0.0127, reference S-13 with Φ = 1.00) 0.02; MS (FAB^+) *m*/*z* (%) 1670.8 (100) [M^+ + H], 1669.9 (59) [M^+]. Anal. Calcd for $C_{68}H_{74}N_4O_6$ (1042.6): C, 78.28; H, 7.15; N, 5.37. Found: C, 78.26; H, 7.09; N, 5.24.



Dye 18. 2,10-Bis(1-hexylheptyl)furo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d*′*e*′*f*′]diisoquinoline-1,3,5,7,9,11(2*H*,10*H*)-hexone (**2**, 401 mg, 0.472 mmol) and (*P*)(+) 6,6′-dimethylbiphenyl-2,2′-diamine (50.1 mg, 0.236 mmol) in quinoline (1.5 mL) were heated at 160 °C for 12 h, allowed to cool, treated with 2 M aqueous HCl (20 mL), and extracted three times with chloroform (3 × 80 mL). The combined organic phases were dried with magnesium sulfate, evaporated, and purified by column separation (silica gel 40–63 μm, toluene, first yellow fluorescent band): Yield 370 mg (83%) yellow solid, mp >300 °C; R_f (silica gel, chloroform) 0.83; IR (ATR) $\tilde{\nu}$ = 2953.4 (m), 2925.5 (m), 2856.1 (m), 2349.7 (w), 1772.6 (w), 1713.2 (s), 1662.1 (vs), 1625.8 (w), 1595.2 (w), 1523.6 (w), 1458.3 (w), 1414.3 (w), 1364.6 (s), 1317.9 (s), 1277.6 (w), 1211.2 (w), 1164.2 (w), 1102.3 (w), 972.1 (w), 942.0 (w), 846.1 (w), 812.3 (w), 766.4 (w), 748.3 (w), 659.4 cm^{-1} (w); ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS) δ = 0.82–0.88 (m, 24 H, 8 × CH_3), 1.24–1.40 (m, 64 H, 32 × CH_3), 1.93–2.05 (m, 8 H, 4 × β-CH_2), 2.31–2.43 (m, 8 H, 4 × β-CH_2), 2.61 (s, 6 H, 2 × CH_3), 5.30–5.38 (m, 4 H, 2 × NCH), 7.04–7.09 (m, 2 H, 2 × $CH_{aromat.}$), 7.41 (t, ^3J(H,H) = 7.7 Hz, 2 H, 2 × $CH_{aromat.}$), 7.65 (d, ^3J(H,H) = 7.5 Hz, 2 H, 2 × $CH_{aromat.}$), 9.00–9.29 (m, 10 H, 10 × $CH_{perylene}$), 9.45 (d, ^3J(H,H) = 8.0 Hz, 4 H, 2 × $CH_{perylene}$), 9.48 (d, ^3J(H,H) = 8.4 Hz, 4 H, 2 × $CH_{perylene}$), 9.48–9.75 (m, 6 H, 6 × $CH_{perylene}$), 10.31–10.35 ppm (m, 4 H, 2 × $CH_{perylene}$); ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS) δ = 14.0, 20.6, 22.6, 27.0, 28.9, 29.2, 30.9, 31.8, 32.5, 123.8, 124.0, 125.3, 126.4, 127.2, 127.8, 128.4, 128.5, 129.6, 131.7, 133.6, 136.0, 141.4, 166.0, 169.6, 206.9 ppm; UV/vis ($CHCl_3$)

λ_{max} (ε) = 382.3 (73900), 412.4 (28000), 438.7 (70900), 470.3 nm (110900); fluorescence ($CHCl_3$, λ_{exc} = 439 nm) λ_{max} (I_{rel}) = 479.5 (1.00), 512.9 (0.62), 548.8 nm (0.18); fluorescence quantum yield ($CHCl_3$, λ_{exc} = 439 nm, $E_{439nm/1cm}$ = 0.0124, reference S-13 with Φ = 1.00) 0.27; MS (MALDI$^+$, anthracene) *m*/*z* (%) 1873.1 [M^+ + H], 1872.1 [M^+]. Anal. Calcd $C_{122}H_{132}N_6O_{12}$ (1872.9): C, 78.18; H, 7.10; N, 4.48. Found: C, 78.24; H, 7.12; N, 4.35.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data of **8** and **10**. 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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■ DEDICATION

Dedicated to Prof. Heinrich Nöth on the occasion of his 85th birthday.

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