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Laterally Extended Naphthalene Tetracarboxylic Bisimides

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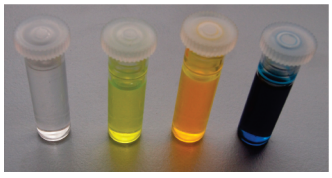
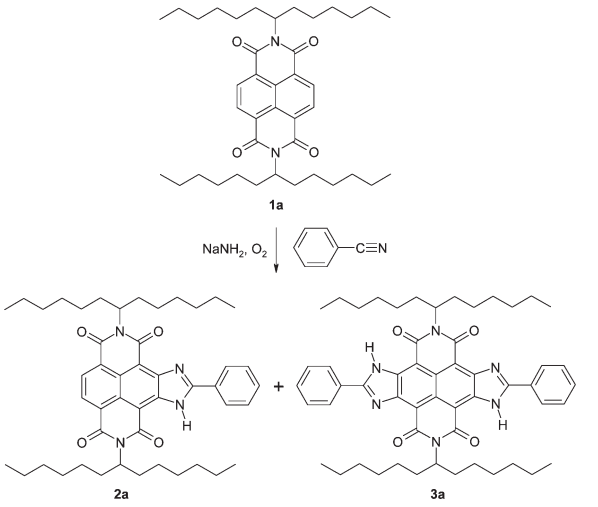


The colorless naphthalene tetracarboxylic bisimides were laterally extended with imidazole rings to give colored and highly fluorescent materials. Donor-substituted phenyl groups at the imidazole rings cause further bathochromic shifts in fluorescence where the strong solvent influence in the spectra is typical for a TICT process. Applications are discussed.

Naphthalene tetracarboxylic bisimides[1] (**1**) with aliphatic *N* substituents are colorless materials and may be applied as white pigments.[2] Many attempts were made to shift their absorption into the visible[1a,3] such as the substitution of the aromatic core with a single or with several donor groups, preferently in the positions 2,7 and 2,6. A ring closure between donor groups in the positions 2 and 3 was described where bathochromic absorption of such materials was observed. The lateral extension of **1** by means of a heterocyclic annellation is still lacking.

We attached the solubility increasing 1-hexylheptyl substituent[4] (swallow-tail substituent) to the nitrogen atoms of naphthalene tetracarboxylic bisimide to form **1a** and allowed the reaction with sodium amide in the dipolar aprotic benzonitrile in the presence of atmospheric oxygen in analogy to perylenetetracarboxylic imides.[5] A substitution of the aromatic core of **1a** proceeded two times at vicinal positions with the incorporation of benzonitrile to form the imidazole derivative **2a**. The lateral extension proceeds even a second time to form the bis-imidazole derivative **3a** with two lateral extensions. The formation of **3a** becomes dominating for a high concentration of sodium amide, whereas appreciable amounts of **2a** are formed for higher dilution. Benzonitrile and sodium amide form 2,4,6-triphenyl-*s*-triazine as a byproduct; however, this can be removed without problems.



The lateral extensions of **1** are not limited to the application of benzonitrile, but can be extended to further substituted nitriles. A melt of 2-naphthonitrile forms predominantly **3b**, whereas **2b** can be obtained with the application of comparably high diluted sodium amide; the structure of **2b** is unambiguous because of its characteristic UV/vis spectrum; however, a full characterization was not successful due to the low yield. The lateral extension proceeds even with the electron-rich 1-dimethylamino benzonitrile to form **2c** and **3c**; however, the purification proved to be more tedious.

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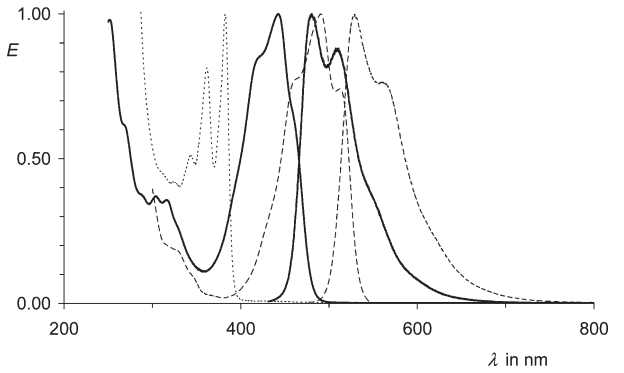

FIGURE 1. UV/vis spectra in chloroform: **1a**, dotted line; **2a**, solid line; and **3a**, dashed line. Left: absorption; right: fluorescence.

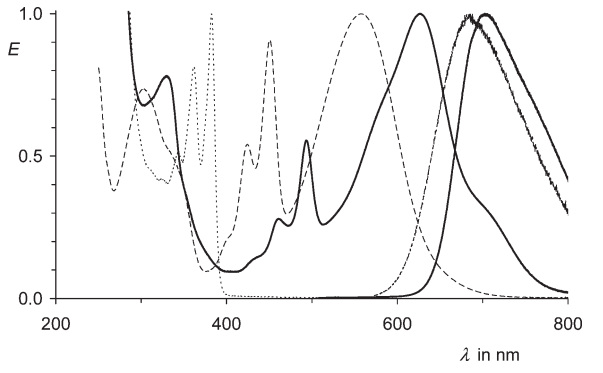

FIGURE 2. UV/vis spectra in chloroform: **1a**, dotted line; **2c**, dashed line; and **3c**, solid line. Left: absorption; right: fluorescence.

The hypsochromic absorption of **1** is shifted bathochromically into the visible by the lateral extension of **2a** to form yellow solutions (see Figure 1). Moreover, the very weak fluorescence of **1a** becomes intensified in **2a** so that green shining solutions are obtained with a fluorescence quantum yield of 28% (Figure 2). The second lateral extension in **2a** causes a further bathochromic shift in **3a** so that orange solutions are formed with a yellow fluorescence of 53% quantum yield. The extension of the side chain in **2b** causes a further bathochromic shift of some 10 nm. The shift in the fluorescence is slightly larger.

The introduction of the electron donating dimethylamino group into the side chain in **2c** and **3c**, respectively, causes appreciable further bathochromic shifts both in absorption and fluorescence so that blue solutions with a strong red fluorescence are obtained for **3c**. The UV/vis spectra of **3c** are noticeably solvent dependent being shown for mixtures of 1-butanol as the polar component and toluene with lower polarity in Figure 3. The absorption of **3c** exhibits a positive solvatochromism where continuous bathochromic shifts with increasing solvent polarity were obtained. The induced bathochromic shift as a function of the molar concentration of the polar component can be described[6] by a relation between the molar energy of excitation (E_T) and a logarithmic function (ln ($c/c^* + 1$) of the molar concentration c of the more polar component such as for other polarity probes; see the insert in Figure 3.

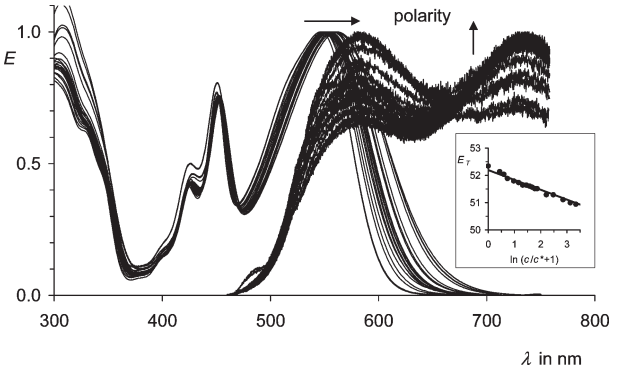

FIGURE 3. Solvatochromism of **2c** in toluene with increasing amounts of 1-butanol as the more polar component. Left: absorption; right: fluorescence. Insert: Analysis of the solvatochromism in absorption where the molar energy of excitation (E_T) is plotted versus ln ($c/c^* + 1$) with c as the molar concentration of 1-butanol and c^* a constant of 0.2 mol·L^{-1}; correlation number $r = -0.98$ with 22 points.

A completely different behavior is observed for the fluorescence because obviously two different species are involved where the hypsochromically fluorescent species dominates in solutions with lower polarity and the bathochromically absorbing one in the more polar 1-butanol. We interpret these results with the formation of TICT states[7] (twisted intramolecular charge transfer) being typical for dimethylamino groups. These states are stabilized in more polar media and are becoming dominating there. As a consequence, the Stokes' shift increased with the solvent polarity because the absorption is less influenced by these effects than fluorescence. Large Stokes' shifts are of special interest for many applications of fluorescence dyes such as for lasers and in analytics because of the suppressed reabsorption of the fluorescence light.

We may presume that naphthalene tetracarboxylic bisimides **1** can be efficiently laterally extended with imidazole rings by the treatment with sodium amide and benzonitrile to form bathochromically absorbing and fluorescent chromophores. The introduction of dimethylamino groups increases not only a further bathochromic shift, but also forms TICT states in polar media with increased Stokes' shifts.

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Experimental Section

***N,N′*-Bis-1-hexylheptylnaphthalenetetracarboxylic-1,8:4,5-biscarboximide (1a).** Naphthalenetetracarboxylic-1,8:4,5-bisanhydride (3.00 g, 11.2 mmol) and 1-hexylheptylamine (5.58 g, 28.0 mmol) were suspended in DMF (100 mL), and the resulting mixture was stirred at 110 °C for 4 h (complete dissolution of all components), allowed to cool to room temperature, quenched by the addition of hydrochloric acid (2 N, 200 mL), extracted with chloroform (3 × 200 mL), dried with magnesium sulfate, evaporated, purified by column separation (silica gel, chloroform), evaporated, and allowed to crystallize (viscous, very slowly crystallizing, orange oil). Yield 5.63 g (79.7%) of a nearly colorless solid, mp 67−68 °C. R_f (silica gel, chloroform) 0.79. IR (ATR) $\tilde{\nu}$ 2922 (m), 2854 (m), 2361 (w), 2338 (w), 1702 (s), 1660 (vs), 1577 (m), 1452 (m), 1398 (w), 1326 (vs), 1245 (s), 1213 (w), 1186 (w), 1092 (w), 887 (vw),773 (m) 733 (w) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.80 (t, ^3J = 7.1 Hz, 12 H, CH_3), 1.11−1.35 (m, 32 H, CH_2), 1.78−1.86 (m, 4 H, β-CH_2), 2.12−2.23 (m, 2 H, β-CH_2), 5.09−5.18 (m, 2 H, CH-N), 8.64−8.76 ppm (br, 4 H, CH_{aryl}). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 14.2, 22.8, 27.1, 29.4, 31.9, 32.5, 55.4, 127.0, 130.8, 131.6, 163.2, 164.4 ppm. UV/vis ($CHCl_3$) λ_{max} (E_{rel}) 342.8 (0.52), 361.6 (0.82), 382.4 nm (1.00). MS (DEI$^+$, 70 eV) *m/z* (%) 632.4 (4.6), 631.4 (19.9), 630.4 (47.8) [M^+], 452.2 (3.1), 451.2 (19.1), 450.2 (89.4), 449.2 (100.0) [$M^+ - C_{13}H_{24}$], 269.0 (6.4), 268.0 (31.27), 267.0 (29.6) [$M^+ - C_{26}H_{50}$]. HRMS ($C_{40}H_{58}N_2O_4$) *m/z* calcd 630.4397, found 630.4389, Δ = −0.0018.

***N,N′*-Bis-1-hexylheptyl-2-phenylimidazolo[4,5:*b*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (2a) and *N,N′*-Bis-1-hexylheptyl-bis-2,2′-phenylimidazolo[4,5:*b*;4,5:*e*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (3a).** *N,N′*-Bis-1-hexylheptylnaphthalenetetracarboxylic-1,8:4,5-biscarboximide (**1a**, 300 mg, 0.476 mmol) and sodium amide (99% powder, 300 mg, 7.69 mmol) were dispersed in benzonitrile (20 mL), and the resulting solution was heated at 165 °C (color change to reddish orange), stirred at 165 °C for 2 h, allowed to cool, evaporated in medium vacuum, treated with aqueous HCl (2 N, 50 mL), extracted with chloroform (3 × 50 mL), dried with magnesium sulfate, filtrated, and purified by column separation (silica gel, chloroform/isohexane 3:1).

First Fraction: *N,N′*-Bis-1-hexylheptyl-2-phenylimidazolo[4,5:*b*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (2a). Yield 44 mg (12%), yellowish, viscous oil. R_f (silica gel, chloroform/isohexane 3:1) 0.47. ^1H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.79 (t, ^3J = 7.0 Hz, 12 H, CH_3), 1.12−1.40 (m, 32 H, CH_2), 1.84−1.94 (m, 4 H, β-CH_2), 2.18−2.35 (m, 4 H, β-CH_2), 5.19−5.28 (m, 2 H, CH-N), 7.58−7.67 (m, 3 H, CH_{aryl}), 8.41 (d, ^3J = 7.0 Hz, 2 H, CH_{aryl}), 8.69−8.79 ppm (br, 2 H, $CH_{naphthalene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 14.3, 22.8, 27.3, 29.5, 30.4, 31.7, 32.0, 32.7, 55.2, 55.5, 124.2, 127.8, 128,7, 129.5, 130.3, 133.2, 161.9, 163.7, 164.9 ppm. UV/vis ($CHCl_3$) λ_{max} (E_{rel}) 251.8 (0.98), 304.0 (0.37), 316.6 (0.36), 442.4 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 417 nm) λ_{max} (I_{rel}) = 480.5 (1.00), 507.6 nm (0.88). Fluorescence quantum yield (λ_{exc} = 417 nm, $E_{417\ nm/1\ cm}$ = 0.0281, $CHCl_3$, reference 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone, RN 110590-84-6, with Φ = 1.00) Φ = 0.28. HRMS ($C_{32}H_{38}N_2O_3$) *m/z* calcd 746.4771, found 746.4761, Δ = −0.0010.

Third Fraction: *N,N′*-Bis-1-hexylheptyl-bis-2,2′-phenylimidazolo-[4,5:*b*;4,5:*e*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (3a). Yield 230 mg (56.0%), orange solid, mp ≥250 °C. R_f (silica gel, chloroform/isohexane 3:1):0.28. IR (ATR) $\tilde{\nu}$ 3409 (s), 2952 (m), 2923 (s), 2854 (m), 1702 (s), 1671 (w), 1640 (vs), 1540 (m), 1460 (vs), 1416 (m), 1329 (w), 1307 (w), 1279 (vs), 1226 (w), 1208 (w), 1190 (m), 1046 (w), 953 (w), 940 (w), 834 (w), 834 (w), 778 (m), 686 (m) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.70−0.90 (m, 12 H, CH_3), 1.13−1.51 (m, 32 H, CH_2), 1.92−2.01 (m, 4 H, β-CH_2), 2.31−2.40 (m, 4 H, β-CH_2), 5.32−5.39 (m, 2 H, CH-N), 7.62 (t, ^3J = 6.8 Hz, 6 H, CH_{aryl}), 8.43 ppm (d, ^3J = 6.6 Hz, 4 H, CH_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 14.3, 22.6, 22.8, 27.4, 29.5, 32.0, 32.7, 55.2, 110.8, 111.5, 121.8, 128.1, 128.7, 129.5, 132.9, 143.4, 161.1, 164.0, 164.8 ppm. UV/vis ($CHCl_3$) λ_{max} (ε) 463.5 (sh, 43400), 492.5 (55010), 512.4 nm (40990). Fluorescence ($CHCl_3$, λ_{exc} = 462 nm) λ_{max} (I_{rel}) = 528.1 nm (1.00). Fluorescence quantum yield (λ_{exc} = 462 nm, $E_{462\ nm/1\ cm}$ = 0.0233, $CHCl_3$, reference 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone, RN 110590-84-6, with Φ = 1.00) Φ = 0.53. HRMS ($C_{54}H_{66}N_6O_4$) *m/z* calcd 862.5146, found 862.5145, Δ = −0.0001. $C_{54}H_{66}N_6O_4$ (863.1) Calcd: C 75.14, H 7.71, N 9.74. Found: C 74.78, H 7.36, N 9.68.

***N,N′*-Bis-1-hexylheptyl-2-(2-naphthyl)imidazolo[4,5:*b*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (2b) and *N,N′*-Bis-1-hexylheptyl-bis-2,2′-(2-naphthyl)imidazolo[4,5:*b*;4,5:*e*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (3b).** *N,N′*-Bis-1-hexylheptylnaphthalenetetracarboxylic-1,8:4,5-biscarboximide (**1a**) (300 mg, 0.476 mmol) and sodium amide (95% powder, 300 mg, 7.69 mmol) were dispersed in 2-naphthonitrile (5 g), and the resulting solution was heated at 165 °C (color change to reddish orange), stirred at 165 °C for 3 h (solidification of the mixture after 2 h), allowed to cool to room temperature, treated with aqueous HCl (2 N, 50 mL), extracted with chloroform (3 × 50 mL), dried with magnesium sulfate, evaporated, and purified by column separation (silica gel, chloroform/isohexane 3:1, removing of the monoadduct and the excess of naphthonitrile, second column separation with chloroform/isohexane 1:1).

First Fraction: *N,N′*-Bis-1-hexylheptyl-2-(2-naphthyl)imidazolo[4,5:*b*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (2b). UV/vis ($CHCl_3$) λ_{max} 445.4 nm. Fluorescence ($CHCl_3$, λ_{exc} = 421 nm) λ_{max} = 505.5 nm. Fluorescence quantum yield (λ_{exc} = 421 nm, $E_{421\ nm/1\ cm}$ = 0.0173, $CHCl_3$, reference 2,9-bis(1-hexylheptyl) anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone, RN 110590-84-6, with Φ = 1.00) Φ = 0.30.

Second Fraction: *N,N′*-Bis-1-hexylheptyl-bis-2,2′-(2-naphthyl) imidazolo[4,5:*b*;4,5:*e*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (3b). Yield 128 mg (28%), deeply red solid, mp ≥250 °C. R_f (silica gel, chloroform/isohexane 1:1) 0.15. IR (ATR) $\tilde{\nu}$ 3413.5 m, 3054.2 w, 2955.0 m, 2921.2 s, 2852.2 s, 2361.8 w, 1698.3 s, 1668.3 w, 1638.6 vs, 1535.3 m, 1496.2 s, 1461.8 vs, 1416.4 m, 1362.5 w, 1326.2 w, 1281.6 vs, 1233.3 m, 1208.5 w, 1197.9 w, 1181.5 m, 1154.5 w, 963.7 w, 949.3 w, 911.1 w, 855.3 m, 819.7 w, 804.1 w, 793.0 w, 751.7 m, 725.5 w, 633.8 w cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.80 (t, ^3J = 6.9 Hz, 12 H, CH_3), 1.14−1.27 (m, 18 H, CH_2), 1.28−1.39 (m, 12 H, CH_2), 1.39−1.51 (m, 4 H, CH_2), 1.97−2.05 (m, 4 H, β-CH_2), 2.35−2.45 (m, 4 H, β-CH_2), 5.36−5.44 (m, 2 H, CH-N), 7.57−7.66 (m, 4 H, $CH_{naphthyl}$), 7.87−7.95 (m, 2 H, $CH_{naphthyl}$), 8.05 (d, ^3J = 8.6 Hz, 4 H, $CH_{naphthyl}$), 8.49 (d, ^3J = 7.9 Hz, 4 H, $CH_{naphthyl}$), 8.97 ppm (s, 2 H, $CH_{naphthyl}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 14.3, 22.8, 27.5, 29.6, 32.0, 32.8, 55.3, 121.9, 124.6, 125.2, 127.5, 128.2, 128.7, 129.4, 129.6, 133.2, 135.5, 161.1, 164.1, 164.9 ppm. UV/vis ($CHCl_3$) λ_{max} (E_{rel}) = 499.4 (1.00), 528.0 nm (0.84). Fluorescence ($CHCl_3$, λ_{exc} = 470 nm) λ_{max} (I_{rel}) = 550.7 nm (1.00). Fluorescence quantum yield (λ_{exc} = 470 nm, $E_{470\ nm/1\ cm}$ = 0.0185, $CHCl_3$, reference 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone, RN 110590-84-6, with Φ = 1.00): Φ = 0.79. HRMS ($C_{62}H_{70}N_6O_4$) *m/z* calcd 962.5459, found 962.5436, Δ = −0.0023. $C_{62}H_{70}N_6O_4$ (963.3) Calcd: C 77.31, H 7.32, N 8.72. Found: C 76.65, H 7.36, N 8.43.

***N,N′*-Bis-1-hexylheptyl-2-(4-dimethylaminophenyl)imidazolo-[4,5:*b*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (2c) and *N,N′*-Bis-1-hexylheptyl-bis-2,2′-(4-dimethylaminophenyl)imidazolo[4,5:*b*;4,5:*e*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (3c).** *N,N′*-Bis-1-hexylheptylnaphthalenetetracarboxylic-1,8:4,5-biscarboximide (**1a**, 300 mg, 0.476 mmol), sodium amide (300 mg, 7.69 mmol), and 4-dimethylaminobenzonitrile (5 g, 34.2 mmol) were allowed to react and purified analogously to **2a** and **3a**.

First Fraction: *N*,*N*′-Bis-1-hexylheptyl-2-(4-dimethylaminophenyl) imidazolo[4,5:*b*]naphthalenetetracarboxylic-1,8:4,5-biscarboximide (2c). Yield 34 mg (9.0%), black powder. R_f (silica gel, chloroform) 0.50. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.80 (t, ^3J = 7.0 Hz, 12 H, CH_3), 1.10−1.46 (m, 32 H, CH_2), 1.82−1.95 (m, 4 H, β-CH_2), 2.16−2.36 (m, 4 H, β-CH_2), 3.15 (s, 6 H, NCH_3), 5.19−5.30 (m, 2 H, α-CH), 6.87 (d, ^3J = 8.3 Hz, 2 H, CH_{aryl}), 8.31 (d, ^3J = 7.9 Hz, 2 H, CH_{aryl}), 8.63−8.75 ppm (m, 2 H, $CH_{naphthyl}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ 14.3, 22.8, 27.3, 29.5, 29.5, 32.0, 32.6, 32.7, 40.7, 55.0, 55.3, 112.4, 114.6, 124.1, 128.8, 129.6, 130.9, 153.4, 162.6, 163.9, 164.8, 165.1 ppm. UV/vis ($CHCl_3$) λ_{max} (E_{rel}) = 303.2 (0.74), 424.6 (0.54), 450.6 (0.91), 558.6 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 451 nm) λ_{max} (I_{rel}) = 684.8 nm (1.00). HRMS ($C_{49}H_{67}N_5O_4$) *m*/*z* calcd 790.5227, found 790.5233, Δ = +0.0006.

Second Fraction: *N*,*N*′-Bis-1-hexylheptyl-bis-2,2′-(4-dimethyl-aminophenyl)imidazolo[4,5:*b*;4,5:*e*]naphthalenetetracarboxylic-1, 8:4,5-biscarboximide (3c). Yield 23 mg (5.1%), black powder, mp > 250 °C. R_f (silica gel, chloroform) 0.12. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.80 (t, ^3J = 6.9 Hz, 12 H, CH_3), 1.10−1.48 (m, 32 H, CH_2), 1.92−2.01 (m, 4 H, β-CH_2), 2.28−2.43 (m, 4 H, β-CH_2), 3.14 (s, 12 H, N-CH_3), 5.30−5.40 (m, 2 H, CH-N), 6.84 (d, ^3J = 8.2 Hz, 4 H, CH_{aryl}), 8.31 ppm (d, ^3J = 8.2 Hz, 4 H, CH_{aryl}). UV/vis ($CHCl_3$) λ_{max} (E_{rel}) = 303.0 (0.78), 460.8 (0.28), 493.6 (0.55), 627.4 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 493. 6 nm): λ_{max} (I_{rel}) = 702.0 nm (1.00). HRMS ($C_{58}H_{77}N_8O_4$) *m*/*z* calcd 949.6068, found 949.6014, Δ = −0.0054.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR of compounds **1a**, **2a**, **2c**, **3a**, **3b**, and ^{1}H NMR of **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.