Supporting information

Self-assembly of Amphiphilic Imidazolium-based Hexa-*peri*-hexabenzocoronenes Into Ordered Nanostructures*

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Characterization

Scheme 1: (i) diphenyl ether, 250 ^{o}C, 68%; (ii) organoboranes obtained from the reaction of 11-chloroundecene with 9-BBN, Pd(dppf)Cl_2, K_2CO_3, 60%; (iii) $FeCl_3$, CH_2Cl_2/CH_3NO_2, 55%; (iv) *N*-methylimidazole, 135 ^{o}C, 78%; (v) NH_4PF_6, water, 91%; (vi) NH_4BF_4, water, 87%.

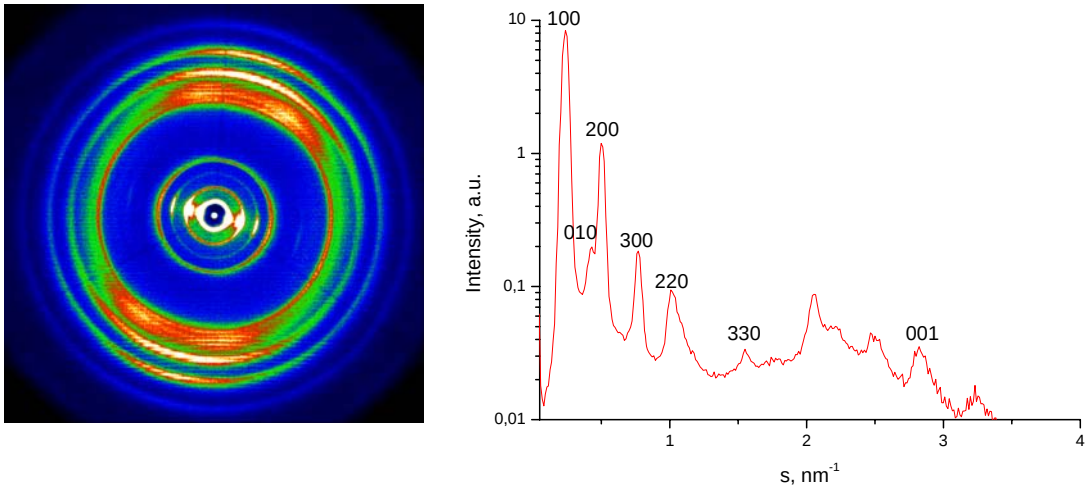

Figure S1: *X-ray diffractogram and intensity distribution pattern for **7** at room temperature.*

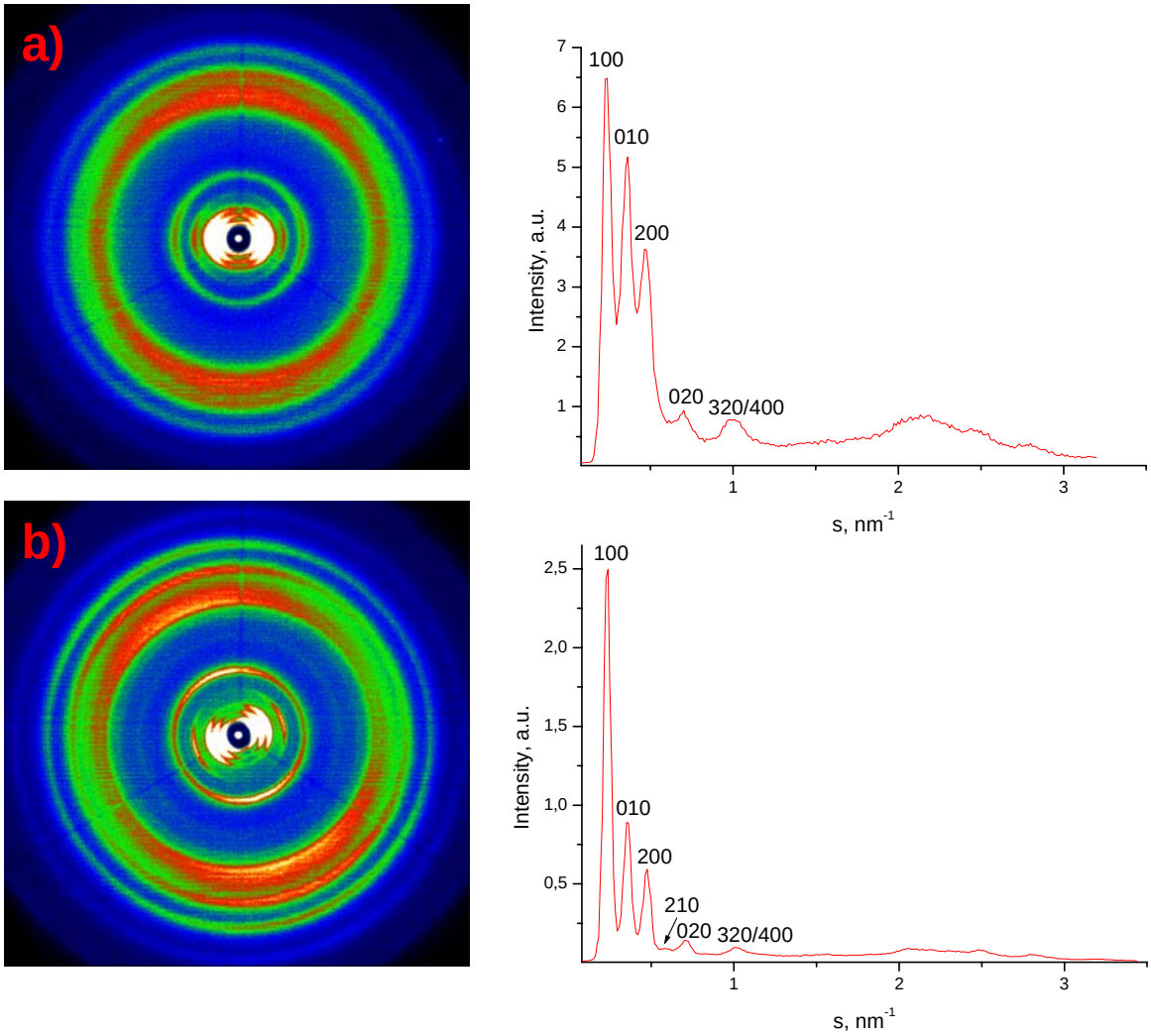

Figure S2: *X-ray diffractogram and intensity distribution pattern for a)* ***1b*** *and b)* ***1c****, at room temperature.*

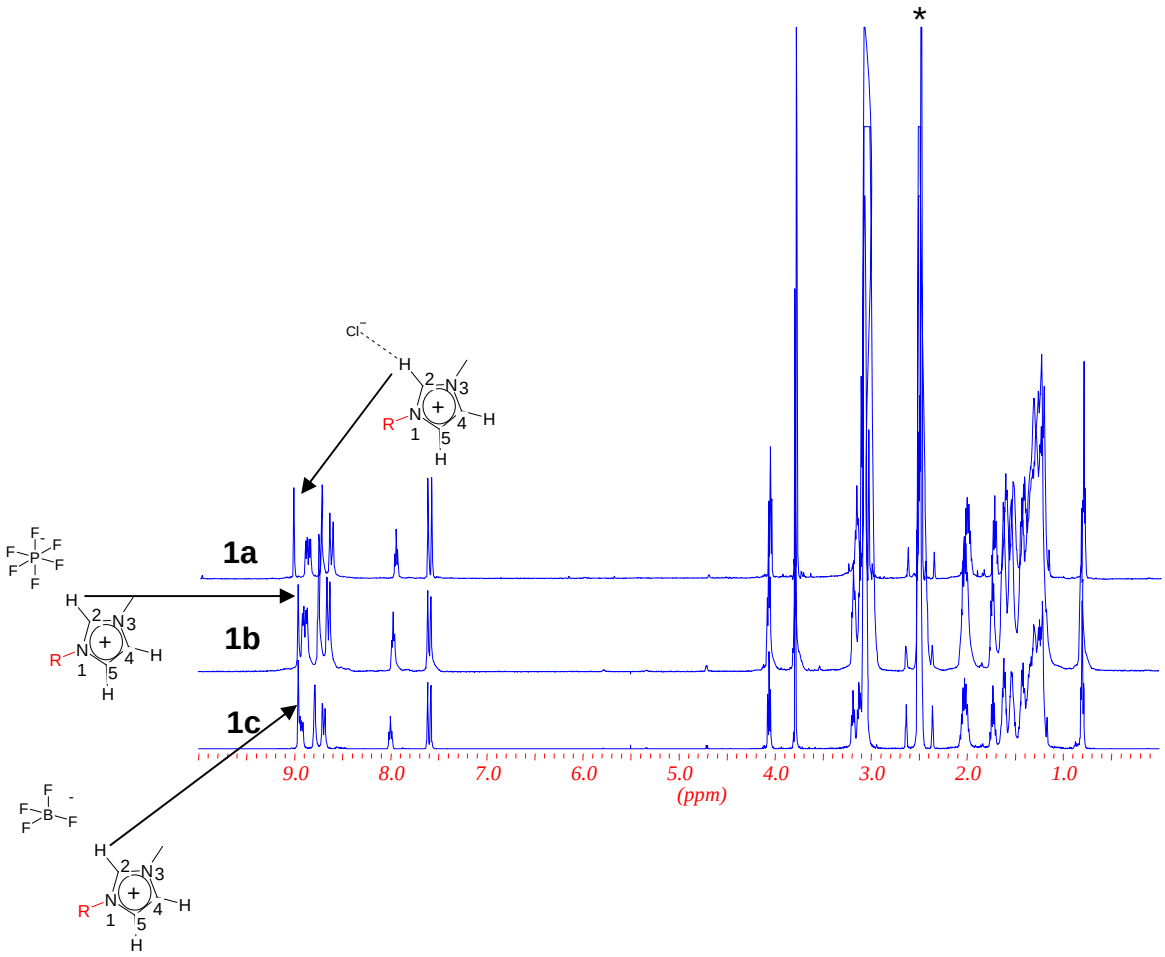

***Figure S3**: [1]H NMR spectra of **1a**, **1b** and **1c** in DMSO at 353 K (C = 1.3x10[-3] mol/L); insets shows the schematical representations of the imidazolium units (C2-H) and points towards their corresponding [1]H NMR chemical shift.*

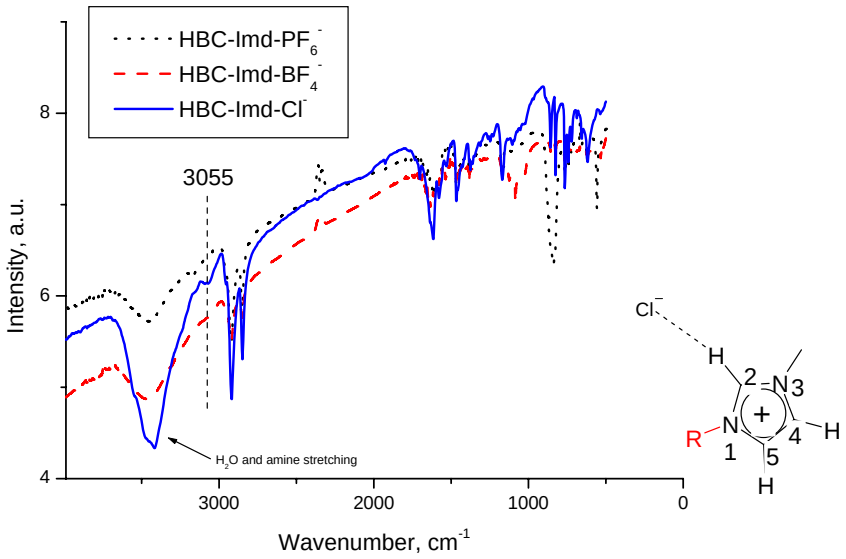

***Figure S-4**: Infrared spectrum of **1a**, **1b** and **1c** in KBr, inset shows a schematical representation of hydrogen bonds of imidazolium with chlorine*

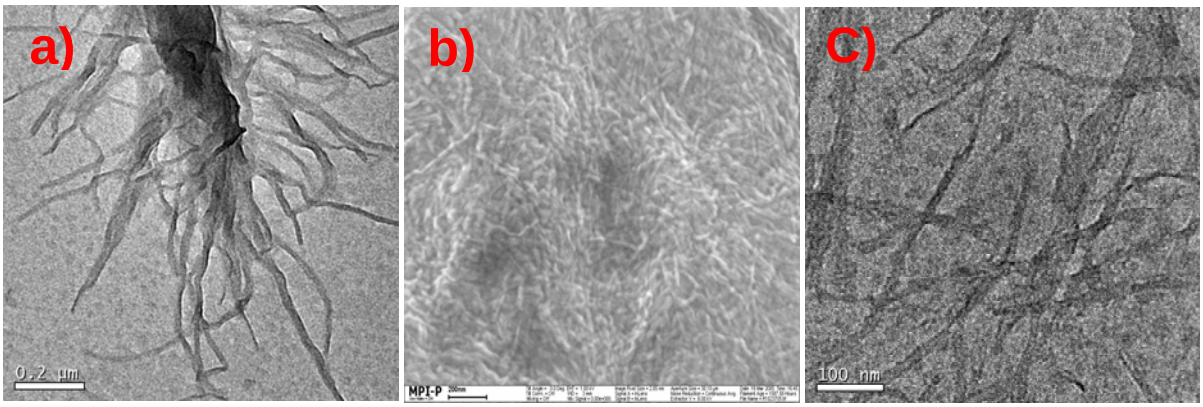

***Figure S5**: a) TEM image of 1a after drop casting of a DMSO solution of **1a** on a silicon oxide substrate and evaporation of solvent; b) SEM picture showing ordered nanofibrillous structures obtained after adding ethanol to the DMSO **1a** solution, drop casting on silicon oxide substrate and evaporation of solvent; c) TEM image of 1a after drop casting DMSO/water solution on silicon oxide surface and solvents evaporation.*

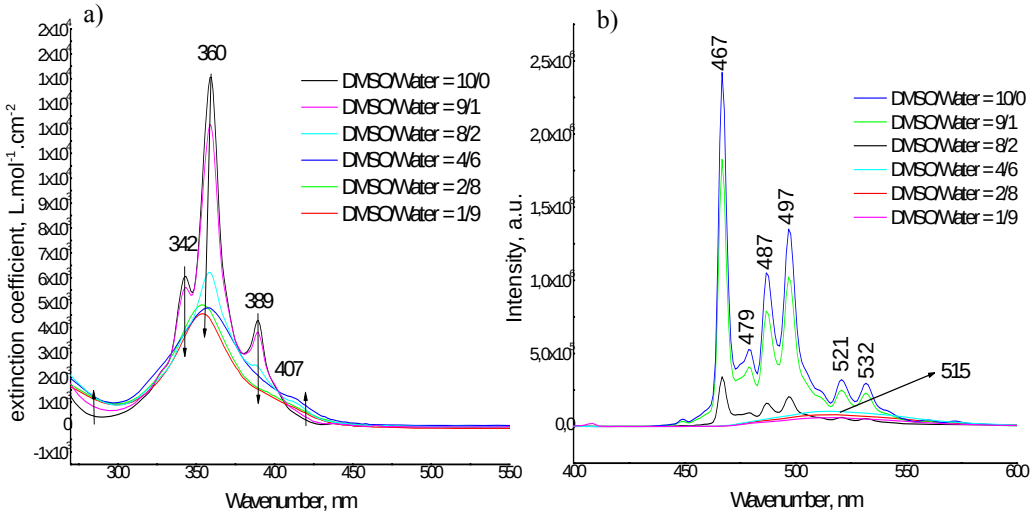

Figure. S6 Water/DMSO solvent dependent spectra a) UV-vis and b) fluorescence of **1a** at 10^{-6} M concentration.

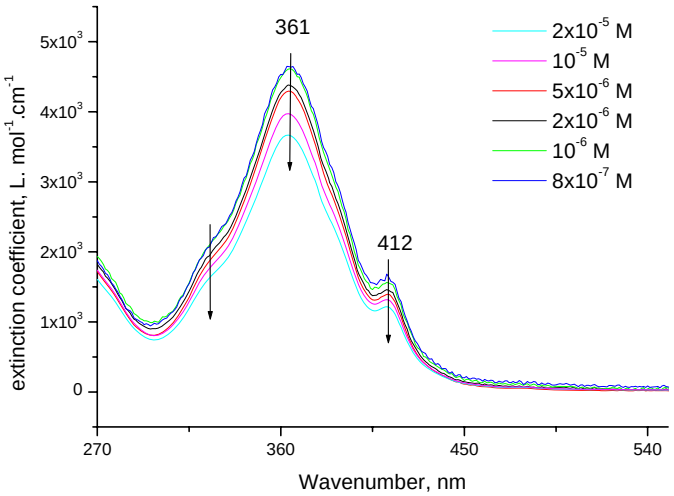

Figure S7*: concentration dependent UV-vis absorption spectrum of* ***1a*** *in 9/1 water/DMSO mixture at room temperature.*

Experimental section:

Compound (5): In a dry 25 ml Schlenk tube, 3,4-bis[(4-dodecyl)phenyl]-2,5-diphenylcyclopentadienone **3** (1g, 1.387 mmol), bis(4-bromophenyl)acetylene **4** (560 mg, 1.664 mmol) and 2.5ml of diphenyl ether were added. The reaction was refluxed overnight under argon. After cooling, product was precipitated from methanol and purification by column chromatography with petroleum ether/dichloromethane (9/1) afforded 970 mg, yield 68%. **^{1}H NMR (250 MHz, CD_2Cl_2, 298K):** δ_{ppm} = 7.07-6.98 (m, 4H, CH_{arom}), 6.93-6.78 (m, 10H, CH_{arom}), 6.77-6.6 (m, 12H, CH_{arom}), 2.39-2.28 (m, 4H, CH_2), 1.6-1.0 (m, 40H, CH_2), 0.95-0.8 (m, 6H, CH_3). **^{13}C NMR (125 MHz, CD_2Cl_2, 298K) :** δ_{ppm} = 141.55, 140.91, 140.84, 140.23, 140.19, 139.06, 138.10, 133.50, 131.75, 131.51, 130.27, 127.10, 127.01, 125.79, 119.91, 35.65, 32.36, 31.59, 30.13, 30.08, 29.89, 29.79, 29.24, 23.11, 14.27. **MS** (FD, 8 kV): *m/z* (%): 1028.8 (100)

[M^+] (calcd for $C_{66}H_{76}Br_2$: 1029.15). **Elemental analysis:** calcd. for $C_{66}H_{76}Br_2$: C, 77.03 H 7.44, Found C, 77.24 H 7.39.

Compound (6): In a dry 100 mL two-necked round-bottomed flask, 4.27 mL of a 0.5 M solution of 9-borabicyclo[3.3.1]nonane (9-BBN) in THF and 11-chloro-1-undecene (367 mg, 1.943 mmol) were mixed under argon atmosphere, and the resulting mixture was stirred overnight at room temperature. To this solution, at first, 0.65 mL of 3M aqueous K_2CO_3 solution was added via a syringe followed after 15 min with (500 mg, 0.485 mmol) of **5** and 40 mg of [$PdCl_2$(dppf)], respectively. The reaction mixture was stirred under argon at room temperature overnight. The product was extracted with CH_2Cl_2, washed with water three times and dried over magnesium sulfate. After evaporating the solvent under vacuum, the residue was purified by column chromatography on silica gel with petroleum ether / CH_2Cl_2 (9:1) to afford **6** (360 mg, 60%) as a waxy material. **^{1}H NMR (500 MHz, CD_2Cl_2, 298K):** δ_{ppm} = 6.87-6.81 (m, 10H, CH_{arom}), 6.73-6.69 (m, 8H, CH_{arom}), 6.65 (d, ^{3}J= 8.03 Hz, 8H, CH_{arom}), 3.54 (t, ^{3}J= 6.08 Hz, 4H, CH_2), 2.35 (t, ^{3}J=7.45 Hz, 8H, CH_2), 1.8-1.73 (m, 4H, CH_2), 1.54-1.06 (m, 72H, CH_2), 0.88 (t, ^{3}J= 6.9 Hz, 6H, CH_3). **^{13}C NMR (125 MHz, CD_2Cl_2, 298K) :** δ_{ppm} = 141.61, 140.78, 139.95, 138.57, 131.95, 131.68, 126.92, 126.79, 125.32, 45.71, 35.66, 33.16, 32.36, 31.62, 30.14, 30.09, 30.01, 29.91, 29.80, 29.34, 29.25, 27.34, 23.12, 14.47. **MS** (FD, 8 kV): *m/z* (%): 1248.0 (100) [M^+] (calcd for $C_{88}H_{120}Cl_2$: 1248.84). **Elemental analysis:** calcd. for $C_{88}H_{120}Cl_2$: C 84.64%, H 9.69%, Found C 84.54%, H 9.74%.

Compound (7): A 250 ml two necked round bottomed flask was charged with 50 mg (0.04 mmol) of and 25 ml of CH_2Cl_2. Using a glass capillary, a constant stream of argon was bubbled through the solution. Then, 117 mg (0.72 mmol) of $FeCl_3$ dissolved in CH_3NO_2 (1.5 ml) was added dropwise using a syringe. After 30 minute, the reaction was quenched with a large excess of methanol. The product was filtrated and washed several times with methanol. The residue was purified using column chromatography on silica gel with petroleum ether/dichloromethane (8/2) and then with toluene as eluents, and dried under vacuum to afford a yellow solid (25 mg, 51%). **^{1}H NMR (250 MHz, THF-d_8, 298K):** δ_{ppm} = 8.79 (d, 4H, CH_{arom}), 8.61,8.59 (2s, 8H, CH_{arom}), 7.87 (t, ^{3}J= 7.9 Hz, 2H, CH_{arom}), 3.46 (t, ^{3}J= 6.68 Hz, 4H, CH_2), 3.08 (t, ^{3}J=7.7 Hz, 8H, CH_2), 2.08-1.92 (m, 8H, CH_2), 1.82-1.08 (m, 68H, CH_2), 0.91-0.81 (m, 6H, CH_3). **^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 343K):** δ_{ppm} = 140.48, 140.44, 129.92, 129.86, 129.79, 125.97, 124.95 123.13, 121.53, 121.46, 121.24, 119.82, 119.68, 45.48, 37.32, 32.96, 32.21, 32.17, 30.18, 30.15, 30.10, 30.08,

30.02, 29.94, 29.91, 29.77, 29.59, 29.19, 27.21, 22.90, 14.31. **MS (MALDI-TOF):** *m/z* (%) = 1236.1 (100) [M^+], (calcd. for $C_{88}H_{108}Cl_2$: 1236.75). **Elemental analysis:** calcd. for $C_{88}H_{108}Cl_2$: C 85.46%, H 8.80%, Found C 85.27%, H 8.95%.

Compound (1a): A dry 25 ml two-neck round flask was charged with 18 mg (0.0145 mmol) of (**7**) and excess of N-methylimidazol (2 ml) were added. The mixture was heated to 135 °C for 24 hours. After cooling, excess of hexane was added. The precipitate was filtered and washed with hexane to afford 15 mg as orange waxy solid in 74% yield. **^{1}H NMR (50 MHz, DMSO, 373K):** δ_{ppm} = 9.01 (s, 2H, CH_{Imid}), 8.95, 8.92 (2d, 4H, CH_{arom}), 8.79, 8.78 (2s, 4H, CH_{arom}), 8.72, 8.70 (2s, 4H, CH_{arom}), 8.00 (t, ^{3}J(H,H)= 7.7 Hz, 2H, CH_{arom}), 7.58 (m, 2H, $H_{e,f}$, CH_{Imid}), 7.55 (m, 2H, CH_{Imid}), 4.06 (t, ^{3}J(H,H)= 7.3 Hz, 4H, CH_2), 3.79 (s, 6H, CH_3), 3.19 (t, ^{3}J(H,H)= 7.6 Hz, 4H, CH_2), 3.14 (t, ^{3}J(H,H)= 7.6 Hz, 4H, CH_2), 2.08-1.08 (m, 76H, CH_2), 0.84-0.78 (m, 6H, CH_3). **^{13}C NMR (125 MHz, DMSO, 393K):** δ_{ppm} =139.70, 139.62, 136.11, 128.62, 128.56, 128.48, 128.39, 125.41, 123.32, 123.02, 121.69, 121.62, 121.44, 120.72, 120.69, 120.59, 118.30, 118.20, 48.44, 35.70, 35.51, 35.17, 30.65, 30.42, 28.76, 28.61, 28.51, 28.48, 28.41, 28.31, 28.03, 27.84, 25.06, 21,33, 13.04. **MS (MALDI-TOF):** *m/z* (%) = 1330.09 (100) [M^+], (calcd. for $C_{96}H_{120}N_4$: 1330.05).

Compound (1b): Prepared as described above for compound **(1a**). yellow precipitate, yield: 78%.**^{1}H NMR (500 MHz, DMSO, 353K):** δ_{ppm} = 8.97 (s, 2H, CH_{Imid}), 8.76 (d, 2H, ^{3}J(H,H) = 8.2 Hz, CH_{arom}), 8.70 (d, 2H, ^{3}J(H,H) = 8.0 Hz, CH_{arom}), 8.59 (s, 4H, CH_{arom}), 8.48, 8.43 (2s, 4H, CH_{arom}), 7.85 (t, ^{3}J(H,H) = 7.6 Hz, 2H, CH_{arom}), 7.63 (t, ^{3}J(H,H) = 1.7 Hz, 2H, CH_{Imid}), 7.59 (t, 2H, ^{3}J(H,H) = 1.7 Hz, CH_{Imid}), 4.04 (t, ^{3}J(H,H) = 7.3 Hz, 4H, CH_2), 3.76 (s, 6H, CH_3), 3.10 (t, ^{3}J(H,H) = 7.6 Hz, 4H, CH_2), 3.00 (t, ^{3}J(H,H) = 7.6 Hz, 4H, CH_2), 2.04-1.13 (m, 76H, CH_2), 0.78 (t, ^{3}J(H,H) = 6.9 Hz, 6H, CH_3). **^{13}C NMR (75 MHz, DMSO, 393K):** δ_{ppm} = 139.78, 139.69, 135.95, 128.68, 128.61, 128.51, 128.42, 125.46, 123.35, 123.05, 121.70, 121.65, 121.46, 120.86, 120.78, 120.65, 118.35, 118.24, 48.48, 35.72, 35.52, 35.17, 30.65, 30.44, 28.73, 28.60, 28.51, 28.49, 28.41, 28.31, 28.03, 27.83, 25.05, 21.34, 13.04. **MS (MALDI-TOF):** *m/z* (%) = 1475.18 (100) (calcd. for $C_{96}H_{120}N_4PF_6$: 1475.00) and 1620.20 (40) (calcd. for $C_{96}H_{120}N_4P_2F_{12}$: 1619.97). **MS (MALDI-TOF):** *m/z* (%) = 143.55 (100) [M^-], (calcd. For (PF_6^-): 144.96).

Compound (1c): Prepared as described above for compound **(1a**). yellow precipitate, yield: 84%. **^{1}H NMR (500 MHz, DMSO, 353K):** δ_{ppm} = 8.98 (s, 2H, CH_{Imid}), 8.76 (d, 2H, $^{3}J(H,H)$ = 7.9 Hz, CH_{arom}), 8.70 (d, 2H, $^{3}J(H,H)$ = 7.4 Hz, CH_{arom}), 8.58 (s, 4H, CH_{arom}), 8.47, 8.41 (2s, 4H, CH_{arom}), 7.84 (t, $^{3}J(H,H)$ = 7.3 Hz, 2H, CH_{arom}), 7.64 (t, $^{3}J(H,H)$ = 1.7 Hz, 2H, CH_{Imid}), 7.60 (t, 2H, $^{3}J(H,H)$ = 1.7 Hz, CH_{Imid}), 4.03 (t, $^{3}J(H,H)$ = 7.3 Hz, 4H, CH_2), 3.76 (s, 6H, CH_3), 3.10 (t (broad), 4H, CH_2), 3.00 (t (broad), 4H, CH_2), 2.04-1.12 (m, 76H, CH_2), 0.77 (t, $^{3}J(H,H)$ = 6.8 Hz, 6H, CH_3). **^{13}C NMR (125 MHz, DMSO, 393):** δ_{ppm} = 139.64, 139.54, 135.92, 128.77, 128.53, 128.43, 128.34, 125.33, 123.28, 123.03, 121.67, 121.59, 121.40, 120.71, 120.65, 120.51, 118.25, 118.14, 48.47, 35.68, 35.47, 35.14, 30.62, 30.36, 28.69, 28.57, 28.48, 28.45, 28,38, 28.27, 27.99, 27.80, 25.03, 21.29, 12.98. **MS (MALDI-TOF):** *m/z* (%) = 1416.06 (100), (calcd. for $C_{96}H_{120}N_4BF_4$: 1415.95) 1503.08 (52) (calcd. for $C_{96}H_{120}N_4B_2F_8$: 1502.95) and 1620.20 (40) (calcd. for $C_{96}H_{120}N_4P_2F_{12}$: 1619.97). **MS (MALDI-TOF):** *m/z* (%) = 85.64 (100) [M^-], (calcd. for (BF_4^-): 86.80).