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Synthesis and properties of 4,4′-bipyridine based tetracationic carbazolophanes

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Abstract—The precyclophane derived from 3,6-bis(bromomethyl)-9-ethylcarbazole and 5 equiv of 4,4′-bipyridine underwent macrocyclization on quaternization with various dibromides including 3,6-bis(bromomethyl)-9-ethylcarbazole to give carbazole-paraquat, self-complementary, cyclophanes revealing distinct charge-transfer and electrostatic interactions. The macrocyclic carbazolophane **1** was also obtained by a one-pot quaternization technique using equimolar amounts of 3,6-bis(bromomethyl)-9-ethylcarbazole and 4,4′-bipyridine.

Interactions between electron donors and complementary electron acceptor groups in cyclophanes can form charge-transfer (CT) complexes and can exhibit π–π interactions in supramolecules.[1,2] Higher aggregated systems such as pseudorotaxanes, rotaxanes, and [*n*]catenanes can be elegantly constructed using this kind of cyclophane.[3] Introduction of the carbazole (Cz) unit into such donor–acceptor molecules is very attractive due to its strong electron donating ability. The design and synthesis of various types of carbazolophanes and their CT studies are known in the literature including [3,3][3,9]carbazolophanes,[4] [2,2]paracyclo(3,6)carbazolophanes,[5] *N*-aryl carbazolophanes,[6] and carbazolopyridinophane.[7] The synthesis and photophysical properties of poly(*N*-vinyl carbazole) doped with electron acceptors such as fullerenes was recently studied by Nishimura and co-workers.[8] It is known that exciplexes are formed between Cz and acceptors, such as terephthalate[9] and dicyanobenzene[10] derivatives. However, to the best of our knowledge, no paraquat based Cz-acceptor cyclophanes have been reported. Herein we wish to report the synthesis of 4,4′-bipyridine based tetracationic carbazolophanes with identical spacers, **1**, and non-identical spacers, **2**–**6**, along with their charge-transfer and electrochemical behavior.

The synthetic pathway leading to the synthesis of precyclophane **8** is outlined in Scheme 1. Dropwise addition of 1 equiv of 3,6-bis(bromomethyl)-9-ethylcarbazole (**7**)[11] with 5 equiv of 4,4′-bipyridine in CH_3CN at 40 °C gave the dicationic precyclophane **8** as an orange colored solid in 68% yield after counter-ion exchange and recrystallization from acetone/H_2O (7:3). In order to increase the yield of the precyclophane **8**, the quaternization reaction was carried out under reflux. However, the reaction mixture turned green indicating decomposition of the dibromide **7** due to its instability at high temperatures. The ^{1}H NMR of **8**[12] showed a triplet at δ 1.25 ($J = 7.3$ Hz) and a quartet at δ 4.44 ($J = 7.3$ Hz) for the *N*-Et unit, a singlet at δ 6.01 for the Cz–CH_2– protons, whilst the Cz protons appeared as a mutiplet at δ 7.71–7.75 integrating for four protons and as a two proton singlet at δ 8.37, in addition to the bipyridinium protons. In the ^{13}C NMR, the *N*-Et carbons appeared at δ 14.2 and δ 39.7 and the Cz–CH_2– carbons at δ 64.3 in addition to the aromatic carbons.

The synthesis of the tetracationic carbazolophane **1** could be achieved either by a one-step or a two-step procedure by quaternization. Reaction of 1 equiv of dibromide **7** with 1 equiv of 4,4′-bipyridine at 40 °C in CH_3CN afforded the tetracationic cyclophane **1** as a deep red solid in a 12% yield. In the two-step procedure, the precyclophane **8** was reacted with a slight excess of the carbazole dibromide **7** under high dilution conditions at 40 °C to give the cyclophane **1** in a 32% yield (Scheme 1). The ^{1}H NMR of carbazolophane **1**[13]

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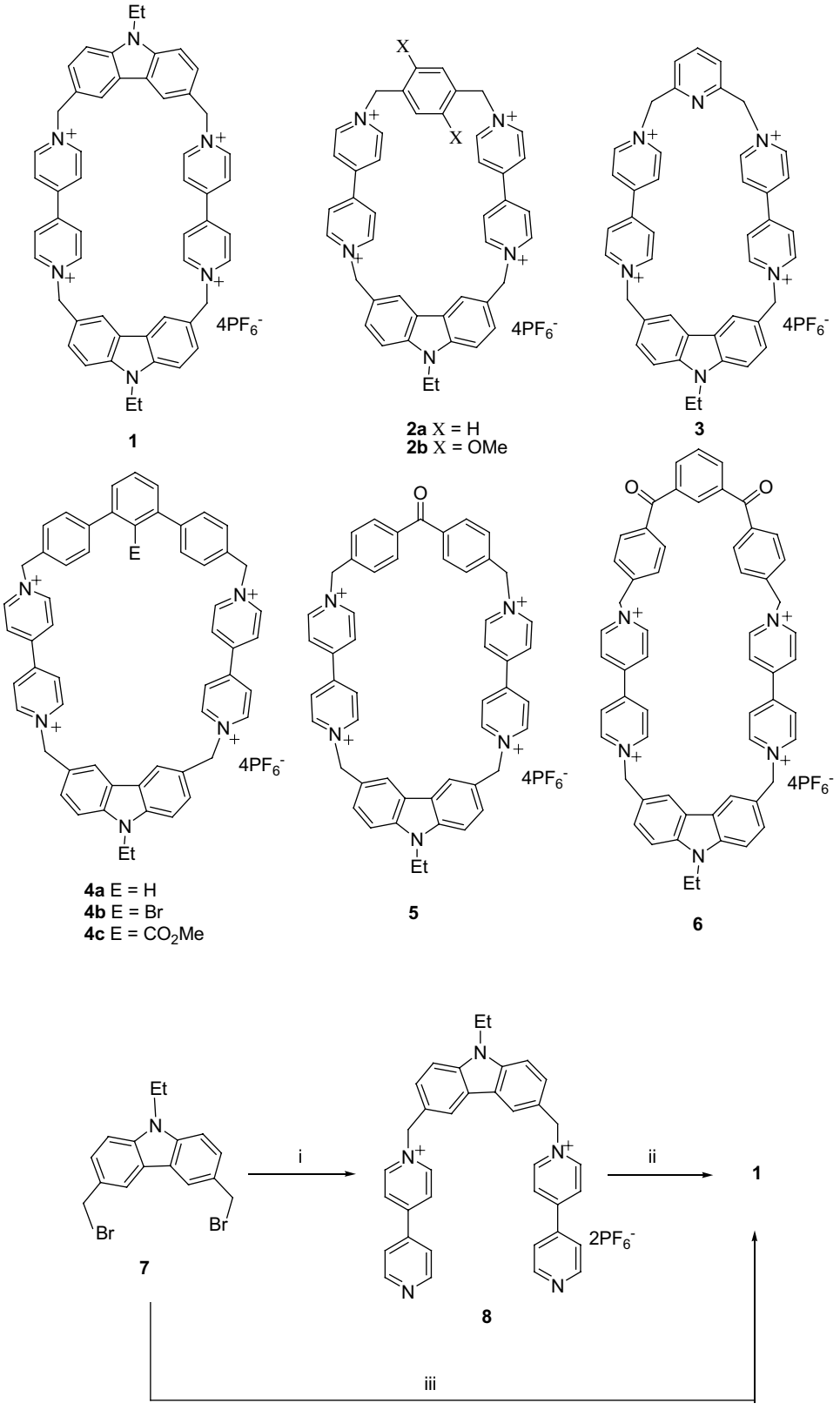


Scheme 1. Reagents and conditions: (i) 4,4′-bipyridine (5 equiv), CH_3CN, 40 °C, 12 h, then NH_4PF_6, CH_3CN, 68%; (ii) **7**, CH_3CN, 40 °C, 48 h, then NH_4PF_6, H_2O, 32%; (iii) 4,4′-bipyridine (1 equiv), CH_3CN, 40 °C, 48 h, then NH_4PF_6, H_2O, 12%.

displayed a triplet at δ 1.26 ($J = 7.1$ Hz) and a quartet at δ 4.45 ($J = 7.1$ Hz) for the *N*-Et unit, a singlet at δ 6.02 for the Cz–CH_2– protons, the Cz protons appeared as two doublets at δ 7.74 ($J = 8.6$ Hz) and at 7.88 ($J = 8.6$ Hz) each integrating for four protons and a four proton singlet at δ 8.09, in addition to the bipyridinium protons. The ^{13}C NMR showed signals at δ 14.4 for the methyl and at δ 39.7 for the methylene carbons

of the *N*-Et unit and at δ 64.7 for the Cz–CH_2– carbons in addition to the aromatic carbons.

In order to test the synthetic utility of precyclophane **8** for the synthesis of tetracationic carbazolophanes, 1 equiv of precyclophane **8** was coupled with 1 equiv of *p*-xylene dibromide (**9a**), 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (**9b**),[14] 2,6-bis(bromomethyl)pyridine (**10**),[15] *m*-terphenyl dibromides **11a–c**,[16] and carbonyl dibromides **12–13**[17] to give the carbazolophanes **2a**, **2b**, **3**, **4a**, **4b**, **4c**, **5**, and **6** in 22%, 18%, 13%, 31%, 25%, 28%, 37%, and 29% yields, respectively, after column chromatography and counter-ion exchange (Scheme 2). The structures of cyclophanes **2–6** were confirmed by spectroscopic and analytical data.[18–23]

The UV–vis absorption spectrum of carbazolophane **1** showed a strong CT absorption band in DMSO with a λ_{max} of 451 nm ($\varepsilon = 1668\ M^{-1}\ cm^{-1}$) and two well resolved absorption peaks located at 340 nm ($\varepsilon = 2056\ M^{-1}\ cm^{-1}$) and at 352 nm ($\varepsilon = 2151\ M^{-1}\ cm^{-1}$) due to transannular π–π electronic interactions between the Cz and the other aromatic rings.[5] Figure 1 shows the CT absorption spectra of cyclophane **1** in various solvents at room temperature. A red shift was observed on changing the solvent from low polarity to higher polarity, but almost the same extinction coefficient ($\varepsilon = 1645$–$1668\ M^{-1}\ cm^{-1}$) was observed.

The presence of neutral and electron rich spacers such as *p*-xylene, 2,5-dimethoxy benzene, pyridine, and *m*-terphenyl in the carbazolophanes **1–4** does not affect the CT absorbance band, which may be due to the high electron donating ability of the carbazole moiety in the cyclophane ring. Introduction of the carbonyl spacers in cyclophanes **5** and **6** resulted in CT band broadening and a red shift in comparison with that of cyclophane **1**. This is due to the high electron affinity of the mono- and dicarbonyl functional groups, in the case of cyclophane **5**, a λ_{max} of 471 nm ($\varepsilon = 1690\ M^{-1}\ cm^{-1}$) and the cyclophane **6** a λ_{max} of 473 nm ($\varepsilon = 1698\ M^{-1}\ cm^{-1}$) were observed.

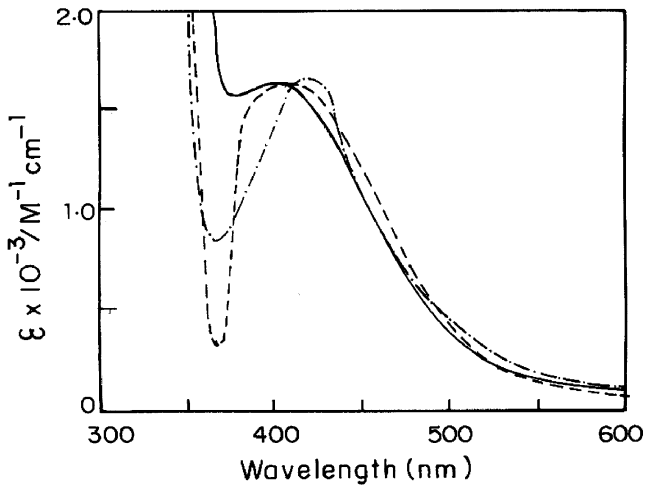
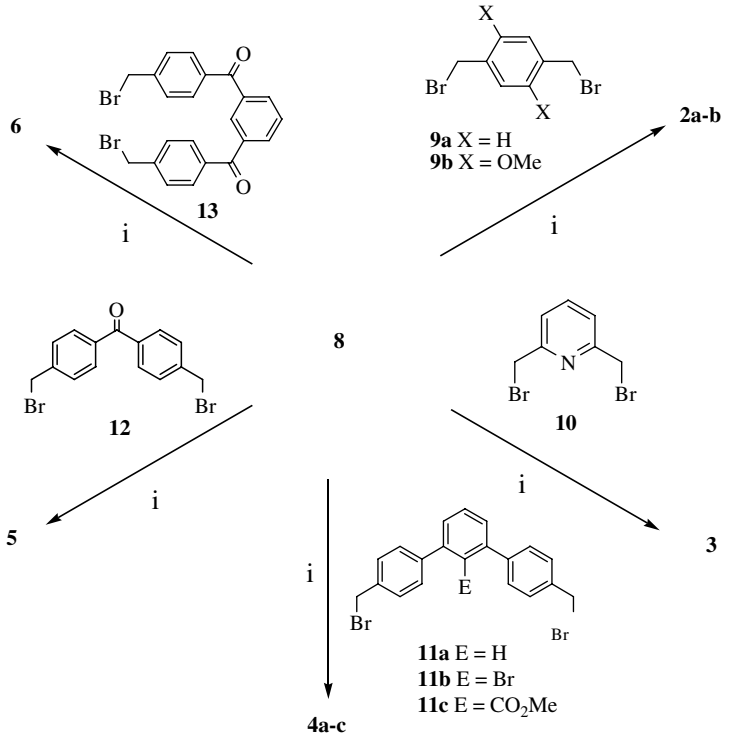


Figure 1. UV–vis absorption spectra of carbazolophane **1** in (i) CH_3CN (—), (ii) CH_3NO_2 (- - -), and (iii) DMSO (– ·).

Half-wave redox potentials versus Ag/AgCl of the cationic carbazolophanes **1–6** were obtained by cyclic voltammetry in DMSO at room temperature. (Scan rate:



Scheme 2. Reagents and conditions: (i) CH_3CN, reflux, 48 h, then NH_4PF_6, H_2O; **2a** (22%), **2b** (18%), **3** (13%), **4a** (31%), **4b** (25%), **4c** (28%), **5** (37%), and **6** (29%).

Table 1. The electrochemical parameters obtained for the cyclophanes in DMSO at 25 °C

Cyclophane	$E^1_{1/2}$ (mV)	ΔE^1_p (mV)	$E^2_{1/2}$ (mV)	ΔE^2_p (mV)
1	−650	137	−950	84
2a	−626	132	−890	112
2b	−631	142	−910	119
3	−628	149	−915	120
4a	−597	151	−980	228
4b	−605	146	−988	232
4c	−590	151	−970	216
5	−585	117	−987	121
6	−634	126	−1036	110

$E^1_{1/2}$ and $E^2_{1/2}$ are the averages of the cathodic and anodic peak potentials of the first and second redox processes, respectively. ΔE^1_p and ΔE^2_p are the differences between the cathodic and anodic peak potentials of the first and second redox processes, respectively.

100 mV s^{-1}, supporting electrolyte: *n*-Bu_4NPF_6, working electrode: glassy carbon, counter electrode: Pt). All the cyclophanes exhibited two sets of redox waves corresponding to $[BIPY]^{4+}/[BIPY]^{2+}$ and $[BIPY]^{2+}/[BIPY]$ redox couples. The electrochemical parameters obtained from the cyclophanes are shown in Table 1.

Compared with ferrocence (for which we found the difference between the anodic and cathodic peaks, $\Delta E_p = 74$ mV vs Ag/AgCl, in DMSO at room temperature), all the redox processes except the second redox processes of cyclophane **1** are quasireversible and the redox potentials were all found to be more negative. The quasireversible nature may be due to the functional groups or non-identical spacers in the cyclophanes.[24] These high negative values of the redox potentials, may be due to minimization of the repulsion between the bipyridinium units. This kind of stabilization decreases the ability of the cyclophanes to accept electrons.[1d] The tetracationic cyclophanes with high negative redox potentials may be used for complexation of both electron rich and electron deficient guest molecules.

In conclusion, we have synthesized various electron rich and electron deficient functionalized tetracationic carbazolophanes with strong electrostatic and CT interactions. The detailed complexation behavior of these cyclophanes is under investigation.

Acknowledgments

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12. Precyclophane **8**: Yield 68%; mp 154 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.25 (t, 3H, $J = 7.3$ Hz); 4.44 (q, 2H, $J = 7.3$ Hz); 6.01 (s, 4H); 7.71–7.75 (m, 4H); 7.95 (d, 4H, $J = 6.2$ Hz); 8.37 (s, 2H); 8.56 (d, 4H, $J = 6.6$ Hz); 8.82 (br s, 4H); 9.31 (d, 4H, $J = 6.6$ Hz): ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.2, 39.7, 64.3, 110.9, 111.0, 122.3, 122.5, 125.2, 126.3, 140.8, 141.5, 145.5, 151.3, 153.2; *m*/*z* (FAB-MS) 678 (M^+-PF_6). Elemental Anal. Calcd for $C_{36}H_{31}N_5P_2F_{12}$: C, 52.50; H, 3.79; N, 8.50. Found: C, 52.59; H, 3.88; N, 8.61.
13. Cyclophane **1**: Yield 32%; mp 210 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.26 (t, 6H, $J = 7.1$ Hz); 4.45 (q, 4H, $J = 7.1$ Hz); 6.02 (s, 8H); 7.74 (d, 4H, $J = 8.6$ Hz); 7.88 (d, 4H, $J = 7.5$ Hz); 8.09 (s, 4H); 8.48 (d, 8H, $J = 6.9$ Hz); 9.25 (d, 8H, $J = 6.9$ Hz); ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.4, 39.7, 64.7, 110.4, 123.0, 125.0, 127.4, 129.5, 141.2, 145.7, 149.4, 162.9; *m*/*z* (FAB-MS) 1189 (M^+-PF_6). Elemental Anal. Calcd for $C_{52}H_{46}N_6P_4F_{24}$: C, 46.79; H, 3.47; N, 6.30. Found: C, 46.88; H, 3.59; N, 6.37.
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18. Cyclophane **2a**: Yield 22%; mp 240 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.27 (t, 3H, $J = 7.3$ Hz); 4.43 (q, 2H, $J = 7.3$ Hz); 5.83 (s, 4H); 6.00 (s, 4H); 7.62–7.71 (m, 6H); 7.86 (d, 2H, $J = 8.4$ Hz); 7.93 (s, 2H); 8.51 (d, 8H, $J = 13.7$ Hz); 9.27 (d, 4H, $J = 6.9$ Hz); 9.41 (d, 4H, $J = 6.9$ Hz): ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.2, 39.8, 63.8, 64.7, 110.2, 121.3, 123.0, 125.4, 127.5, 127.7, 129.3, 130.5, 136.8, 141.1, 145.8, 148.7, 149.4; (FAB-MS) 927 (M^+-2PF_6). Elemental Anal. Calcd for $C_{44}H_{39}N_5P_4F_{24}$: C, 43.40; H, 3.23; N, 5.75. Found: C, 43.55; H, 3.38; N, 5.67.
19. Cyclophane **2b**: Yield 18%; mp 262 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.26 (t, 3H, $J = 7.3$ Hz); 3.81 (s,

6H); 4.42 (q, 2H, $J = 7.3$ Hz); 5.78 (s, 4H); 6.01 (s, 4H); 7.50 (s, 2H); 7.74–7.69 (m, 4H); 7.97 (s, 2H); 8.46 (d, 4H, $J = 6.9$ Hz); 8.51 (d, 4H, $J = 6.9$ Hz); 9.29–9.25 (m, 8H): ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.1, 40.0, 56.8, 64.1, 64.8, 110.2, 115.2, 121.3, 122.9, 125.4, 125.5, 127.2, 127.4, 141.1, 145.8, 145.9, 146.0, 149.2, 151.4, 163.7; (FAB-MS) 987 (M^+-2PF_6). Elemental Anal. Calcd for $C_{46}H_{43}N_5O_2P_4F_{24}$: C, 43.24; H, 3.39; N, 5.48. Found: C, 43.33; H, 3.51; N, 5.57.

20. Cyclophane **3**: Yield 13%; mp 220 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.19 (t, 3H, $J = 7.1$ Hz); 4.36 (q, 2H, $J = 7.1$ Hz); 6.05 (s, 4H); 6.15 (s, 4H); 7.60 (d, 2H, $J = 8.0$ Hz); 7.66–7.71 (m, 3H); 7.91 (d, 2H, $J = 8.0$ Hz); 7.96 (s, 2H); 8.61 (d, 4H, $J = 6.3$ Hz), 8.67 (d, 4H, $J = 6.3$ Hz), 9.44 (d, 4H, $J = 6.9$ Hz), 9.53 (d, 4H, $J = 6.9$ Hz): ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.1, 38.9, 64.0, 64.2, 120.3, 122.5, 125.6, 126.3, 127.2, 127.5, 127.6, 128.0, 140.5, 142.9, 146.4, 146.5, 149.4, 150.2, 152.9; (FAB-MS) 1073 (M^+-PF_6). Elemental Anal. Calcd for $C_{43}H_{38}N_6P_4F_{24}$: C, 42.38; H, 3.14; N, 6.90. Found: C, 42.25; H, 3.26; N, 7.01.
21. Cyclophane **4a**: Yield 31%; mp 190 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.23 (t, 3H, $J = 7.2$ Hz); 4.43 (q, 2H, $J = 7.2$ Hz); 6.08 (s, 4H); 6.85 (s, 4H); 7.24–7.79 (m, 12H); 7.97–8.00 (m, 4H); 8.49 (s, 2H); 8.73 (br s, 8H); 9.60 (br s, 8H): ^{13}C NMR (125 MHz, DMSO-d_6): δ 13.8, 63.3, 64.1, 110.4, 122.5, 122.7, 124.6, 126.0, 126.3, 126.8, 127.3, 127.9, 128.2, 128.7, 129.5, 130.0, 134.0, 140.7, 141.6, 145.2, 145.8, 149.1, 149.4; (FAB-MS) 1224 (M^+-PF_6). Elemental Anal. Calcd for $C_{56}H_{47}N_5P_4F_{24}$: C, 49.10; H, 3.46; N, 5.11. Found: C, 49.27; H, 3.57; N, 5.21.
22. Cyclophane **5**: Yield 37%; mp 270 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.27 (t, 3H, $J = 7.2$ Hz); 4.47 (q, 2H, $J = 7.2$ Hz); 5.97 (s, 4H); 6.08 (s, 4H); 7.36 (d, 4H, $J = 8.6$ Hz); 7.59 (d, 4H, $J = 8.1$ Hz); 7.79–7.81 (m, 4H); 8.31 (s, 2H); 8.62 (d, 4H, $J = 6.9$ Hz); 8.67 (d, 4H, $J = 6.9$ Hz); 9.40 (d, 4H, $J = 6.9$ Hz); 9.43 (d, 4H, $J = 6.9$ Hz): ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.2, 37.8, 64.2, 64.4, 110.1, 121.8, 123.0, 125.2, 127.4, 128.1, 129.6, 130.6, 135.8, 137.8, 139.7, 141.2, 145.8, 146.8, 149.3, 190.3; (FAB-MS) 1176 (M^+-PF_6). Elemental Anal. Calcd for $C_{51}H_{43}N_5OP_4F_{24}$: C, 46.34; H, 3.28; N, 5.30. Found: C, 46.25; H, 3.21; N, 5.39.
23. Cyclophane **6**: Yield 29%; mp 228 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.27 (t, 3H, $J = 7.2$ Hz); 4.42 (q, 2H, $J = 7.2$ Hz); 5.98 (s, 4H); 6.13 (s, 4H); 7.31 (br s, 8H); 7.58 (t, 1H, $J = 7.8$ Hz); 7.70 (d, 2H, $J = 8.8$ Hz); 7.83 (d, 2H, $J = 8.3$ Hz); 7.91 (d, 2H, $J = 7.8$ Hz); 8.18 (s, 2H); 8.27 (s, 1H); 8.69 (br s, 8H); 9.45 (d, 4H, $J = 6.8$ Hz); 9.57 (d, 4H, $J = 6.8$ Hz): ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.8, 37.5, 63.6, 64.3, 109.7, 120.8, 122.8, 125.6, 126.2, 126.9, 127.4, 128.3, 130.1, 130.8, 131.7, 135.2, 135.5, 140.7, 145.4, 145.9, 148.8, 149.3, 150.8, 192.7; (FAB-MS) 1135 (M^+-2PF_6). Elemental Anal. Calcd for $C_{58}H_{47}N_5O_2P_4F_{24}$: C, 48.86; H, 3.32; N, 4.91. Found: C, 48.75; H, 3.19; N, 4.97.
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