Novel Synthesis of Hybrid Calixphyrin Macrocycles.

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Supplementary materials

8 : ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) : δ = 1.93 (s, 12 H, -Me) ; 6.22 (d, *J* = 4.5 Hz, 4H, ***b***-pyr) ; 6.30 (d, *J* = 4.5 Hz, 4H, ***b***-pyr) ; 7.24 to 7.43 (m, 10 H, -Ph) ; 14.10 (s, 2H, -NH-) .

^{13}C NMR (500 MHz, $CDCl_3$, 25°C) : δ = 28.9 ; 29.7 ; 38.2 ; 114.1 ; 127.4 ; 128.3 ; 128.6 ; 130.7 ; 137.2 ; 140.3 ; 140.4 ; 165.3.

UV /Vis (CH_2Cl_2) : λ_{max} (ε) = 322 (14060) ; 422 (51107)

HR-MS (CI) for $C_{36}H_{33}N_4$ ($[M+H]^+$) calcd : 521.2705 ; found : 521.2688

9 : ^{1}H NMR (250 MHz, $CDCl_3$, 25°C) : δ = 1.60 (s, 12H, -Me) ; 1.62 (s, 6H, -Me) ; 5.97 (m, 2H, ***b***-pyr) ; 6.02 (m, 2H, ***b***-pyr) ; 6.29 (d, *J* = 4.2 Hz, 2H, ***b***-pyr) ; 6.35 (d, *J* = 4.2 Hz, 2H, ***b***-pyr) ; 7.33 to 7.36 (m, 5H, -Ph) ; 7.92 (bs, 2H, -NH-), 11.6 (bs, 1H, -NH-).

^{13}C NMR (250 MHz, $CDCl_3$, 25°C) : δ = 28.8 ; 29.5 ; 35.5 ; 37.2 ; 103.3 ; 104.0 ; 114.2 ; 121.2 ; 128.2 ; 129.3 ; 130.6 ; 136.1 ; 137.7 ; 138.7 ; 139.3 ; 139.8 ; 164.8.

UV /Vis (CH_2Cl_2) λ_{max} (ε) : 454 (21058).

HR-MS (CI) for $C_{32}H_{35}N_4$ ($[M+H]^+$) calcd : 475.2861 ; found : 475.2855

Elemental analysis calculated for $C_{32}H_{34}N_4$: C, 80.98, H, 7.22, N, 11.80 (%). Found : C, 80.06, H, 7.15, N, 11.66 (%).

10 : ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) : δ = 1.70 (s, 12H, -Me) ; 5.94 (d, *J* = 2.5 Hz, 2H, ***b***-H), 6.13 (s, 2H, ***b***-H) ; 6.71 (d, *J* = 5 Hz, 2H, ***b***-H) ; 6.79 (d, *J* = 4.5 Hz, 2H, ***b***-H) ; 7.39 to 7.46 (m, 10 H, -Ph) ; 10.7 (s, 1H, -NH-) ; 13.06 (s, 1H, -NH-).

^{13}C NMR (500 MHz, $CDCl_3$, 25°C) : 29.9 ; 38.2 ; 121.4 ; 124.8 ; 127.6 ; 128.8 ; 131.4 ; 135.5 ; 136.5 ; 137.7 ; 137.8 ; 138.7 ; 151.9 ; 182.8.

UV /Vis (CH_2Cl_2) λ_{max} (ε) : 341 (32984) ; 522 (17419).

HR-MS (CI) for $C_{36}H_{33}N_4$ ($[M+H]^+$) *m/z* calcd : 521.2705 ; found : 521.2701.

Elemental analysis calculated for $C_{36}H_{32}N_4$: C, 83.04, H, 6.19, 10.76 %. Found : C, 82.36, H, 6.24, N, 10.65.

11 : ^1H NMR (250 MHz, $CDCl_3$, 25°C) : δ = 1.72 (s, 3H, -Me) ; 1.83 (s, 3H, -Me) ; 2.93 (s, 1H, -OH) ; 6.22 (d, ^2J = 4.2 Hz, 2H, ***b***-H) ; 6.34 (d, ^2J = 4.2 Hz, 2H, ***b***-H) ; 6.40 (d, ^2J = 4.2 Hz, 2H, ***b***-H(c)) ; 6.59 (d, ^2J = 4.2 Hz, 2H, ***b***-H(d)) ; 7.27 to 7.44 (m, 13 H, -Ph) ; 7.78 (m, 2H, H(f)) ; 13.78 (s, 2H, -NH-).

^{13}C NMR (500 MHz, CD_2Cl_2, 25°C) : 24.7 ; 32.6 ; 38.5 ; 77.3 ; 115.1 ; 115.4 ; 126.9 ; 127.9 ; 128.4 ; 128.6 ; 128.9 ; 129.2 ; 129.4 ; 131.1 ; 137.3 ; 140.9 ; 141.2 ; 141.2 ; 141.5 ; 146.1 ; 162.0 ; 166.1.

UV /Vis (CH_2Cl_2) λ_{max} (ε) : 322 (19375) ; 423 (58505)

HR-MS (CI) for $C_{40}H_{33}N_4O$ ($[M+H]^+$) *m/z* calcd : 585.2654 ; found : 5852628.

Elemental analysis calculated for $[C_{40}H_{32}N_4O]\bullet(H_2O)_2$: C, 77.40 ; H, 5.85 ; N, 9.03 %. Found : C, 76.95 ; H, 5.20 ; N, 8.96 (%).

[12ZnCl] : ^1H NMR (250 MHz, $CDCl_3$, 25°C) : δ = 3.12 (s, 3H, -Me) ; 3.10 (s, 3H, -Me) ; 6.37 (d, *J* = 4.6 Hz, 2H, ***b***-H) ; 6.66 (d, *J* = 4.6 Hz, 2H, ***b***-H) ; 6.85 (d, *J* = 4.8 Hz, 2H, ***b***-H) ; 6.97 (d, *J* = 4.8 Hz, 2H, ***b***-H) ; 7.42 (bs, 15H, -Ph).

UV /Vis (CH_2Cl_2) λ_{max} (ε) :360 (28546) ; 406 (34960) ; 433 (36332) ; 715(sh, 9125) ; 787 (20750).

HR-MS (CI) for $C_{40}H_{29}N_4Zn$ ($[M]^+$) *m/z* calcd : 629.1683 ; found : 629.1668.

Elemental analysis calculated for $[C_{40}H_{29}N_4ClZn]\bullet(H_2O)_2$: C, 66.67, H, 4.90, N, 7.78 %. Found : C, 66.49, H, 4.17, N, 7.57.

UV-visible spectra of **8**, **9**, **10** and **11** (CH_2Cl_2, 293 K)