

Supporting Information

Electrochemically fabricated electrochromic films from 4-(*N*-carbazolyl)triphenylamine and its dimethoxy derivative

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List of Contents for Supplementary Material:

Fig. S1 IR spectra of monomers **TPACz** and **MeOTPACz**.

Fig. S2 (a) ¹H and (b) ¹³C NMR spectra of **TPACz** in CDCl₃.

Fig. S3 (a) ¹H and (b) ¹³C NMR spectra of **MeOTPACz** in CDCl₃.

Fig. S4 (a) H-H COSY and (b) C-H HMQC spectra of **TPACz** in DMSO-*d*₆.

Fig. S5 (a) H-H COSY and (b) C-H HMQC spectra of **MeOTPACz** in DMSO-*d*₆.

Fig. S6 UV-Vis absorption and PL spectra of the dilute solutions of (a) **TPACz** and **PTPACz** (b) **MeOTPACz** and **(MeOTPACz)₂** in CH₂Cl₂ (1 x 10⁻⁵ M).

Fig. S7 UV-vis spectra of (a) **TPACz** monomer and (b) **PTPACz** in CHCl₂ solution, and (c) **PTPACz** on the ITO/glass surface.

Fig. S8 Optimized geometry and spatial distributions of the HOMO and LUMO for **TPACz**.

Table S1 Bond lengths [Å] and bond angles [°] for **TPACz** and **MeOTPACz**

Scheme S1 Anodic oxidation pathways of (a) **PTPACz** and (b) **(MeOTPACz)₂**.

Chemical oxidative polymerization

PTPACz could also be prepared by the chemical oxidative polymerization of **TPACz** with FeCl_3 as an oxidant. In a 50-mL two-necked round-bottom flask equipped with a stirring bar under nitrogen atmosphere, a mixture of **TPACz** (0.41 g, 1 mmol), FeCl_3 (0.40 g, 2.5 mmol) in nitrobenzene (2 mL) was stirred at room temperature for 24 h. The reaction mixture was poured into methanol containing 10% hydrochloric acid. The precipitate was collected and washed thoroughly with aqueous ammonium hydroxide. The crude polymer (0.33 g, 80 % yield) was re-dissolved in chloroform. After removing the insoluble fraction by filtration, the filtrate was condensed and poured into methanol. The resulting precipitate was washed with methanol and dried under reduced pressure to yield the polymer **PTPACz** (0.25 g, 61 % yield).

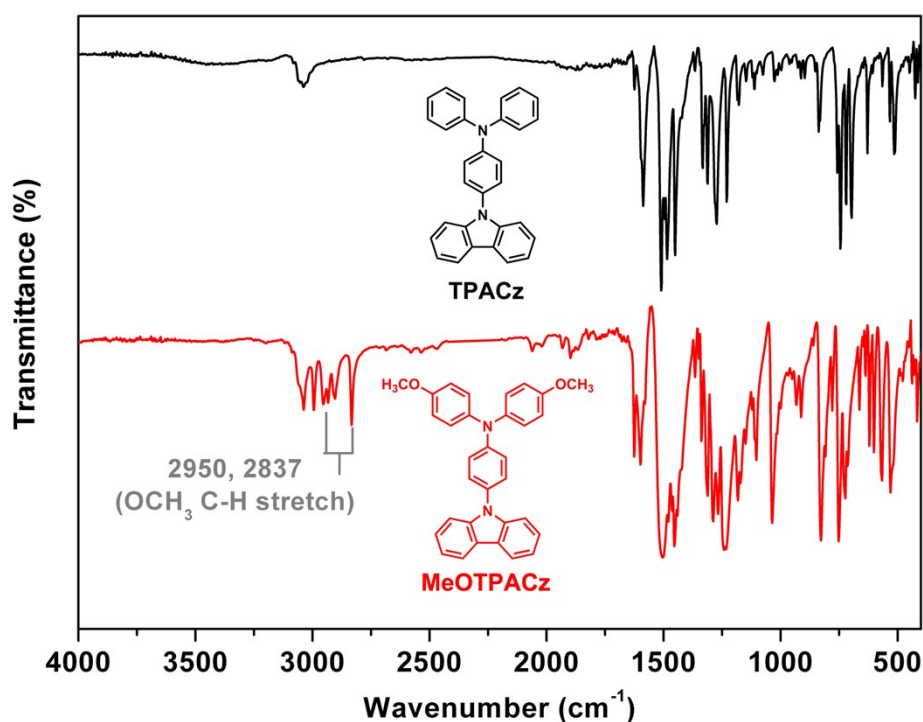


Fig. S1 IR spectra of monomers **TPACz** and **MeOTPACz**.

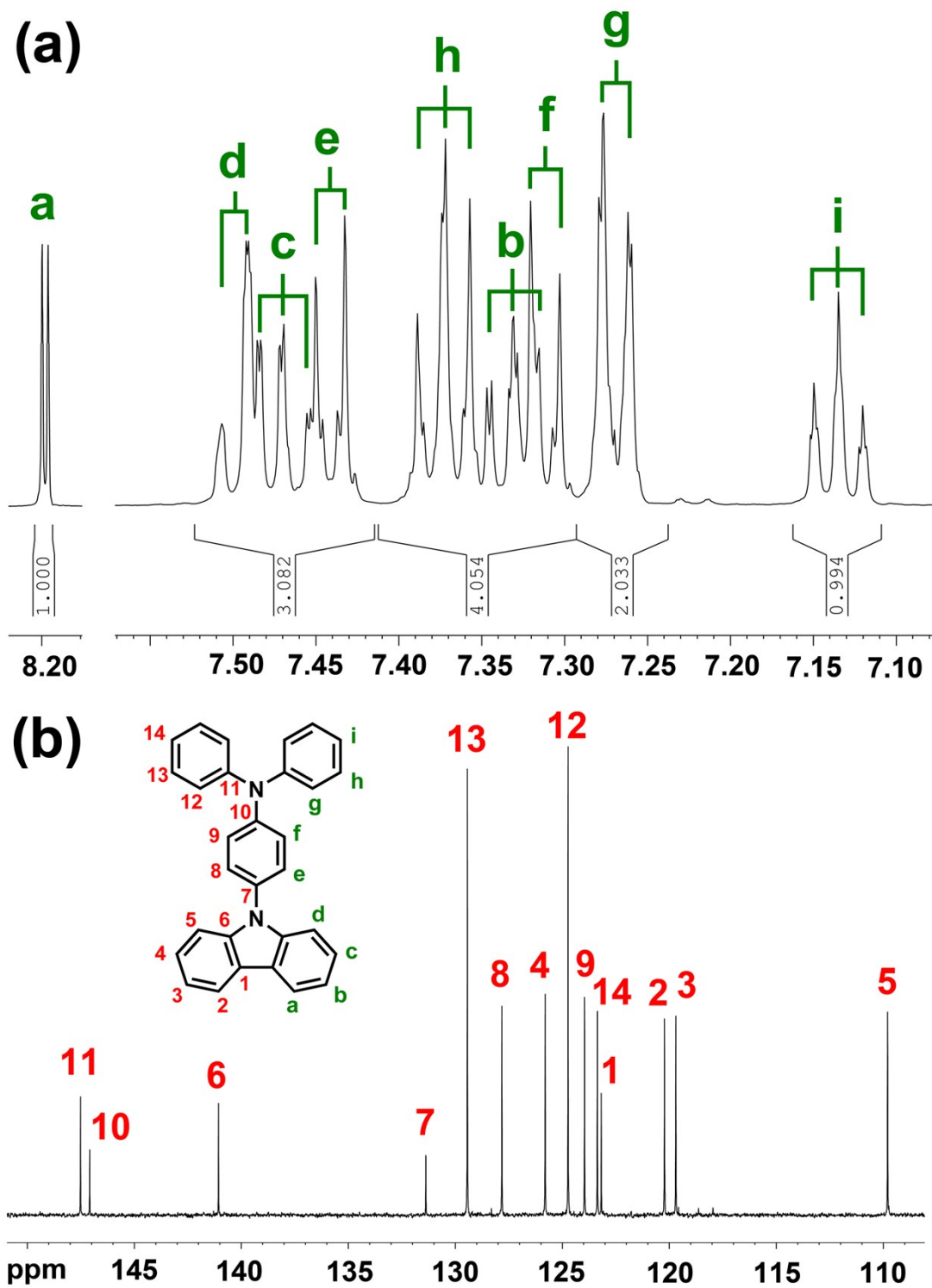
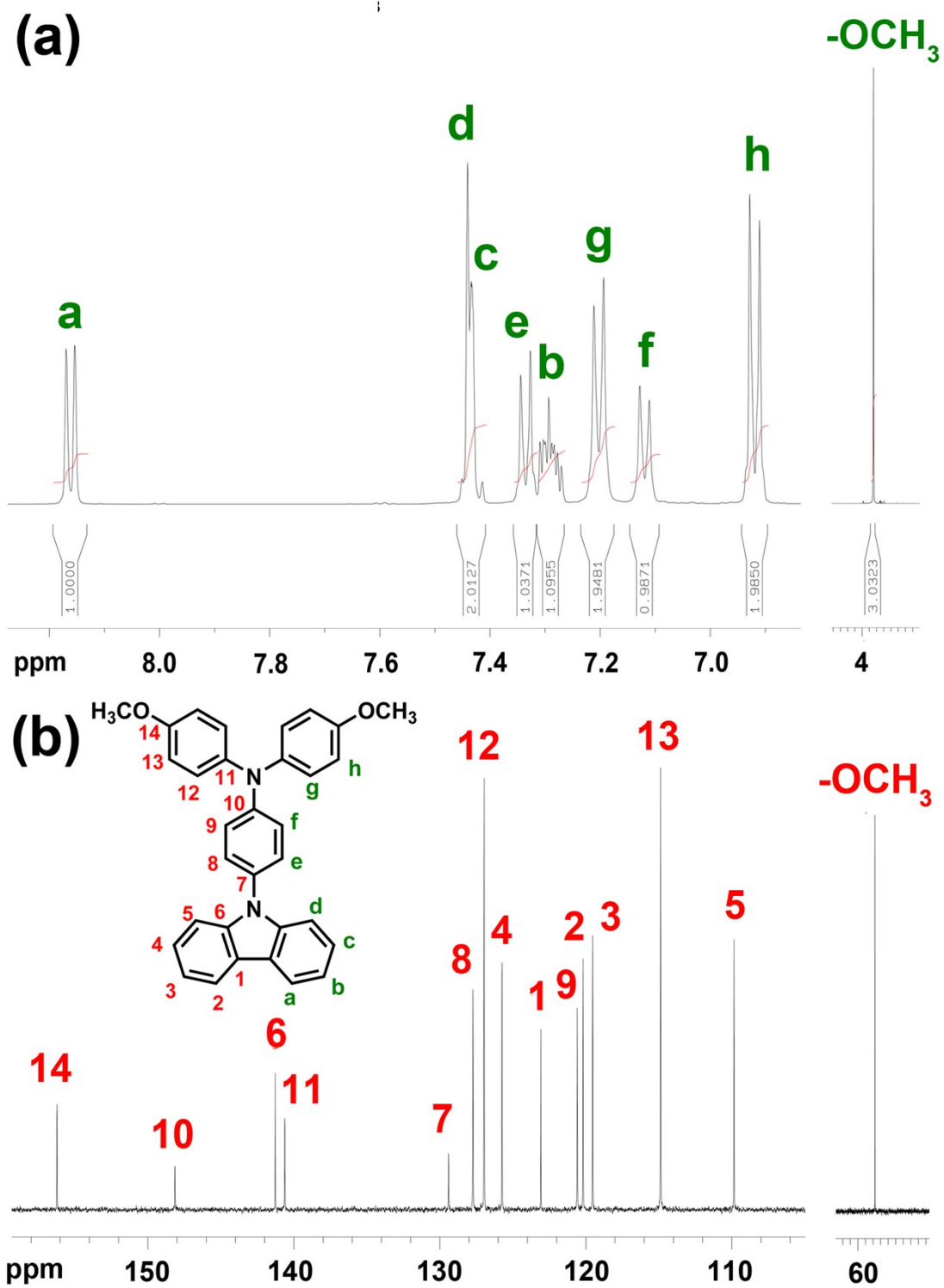


Fig. S2 (a) ^1H and (b) ^{13}C NMR spectra of TPACz in CDCl_3 .



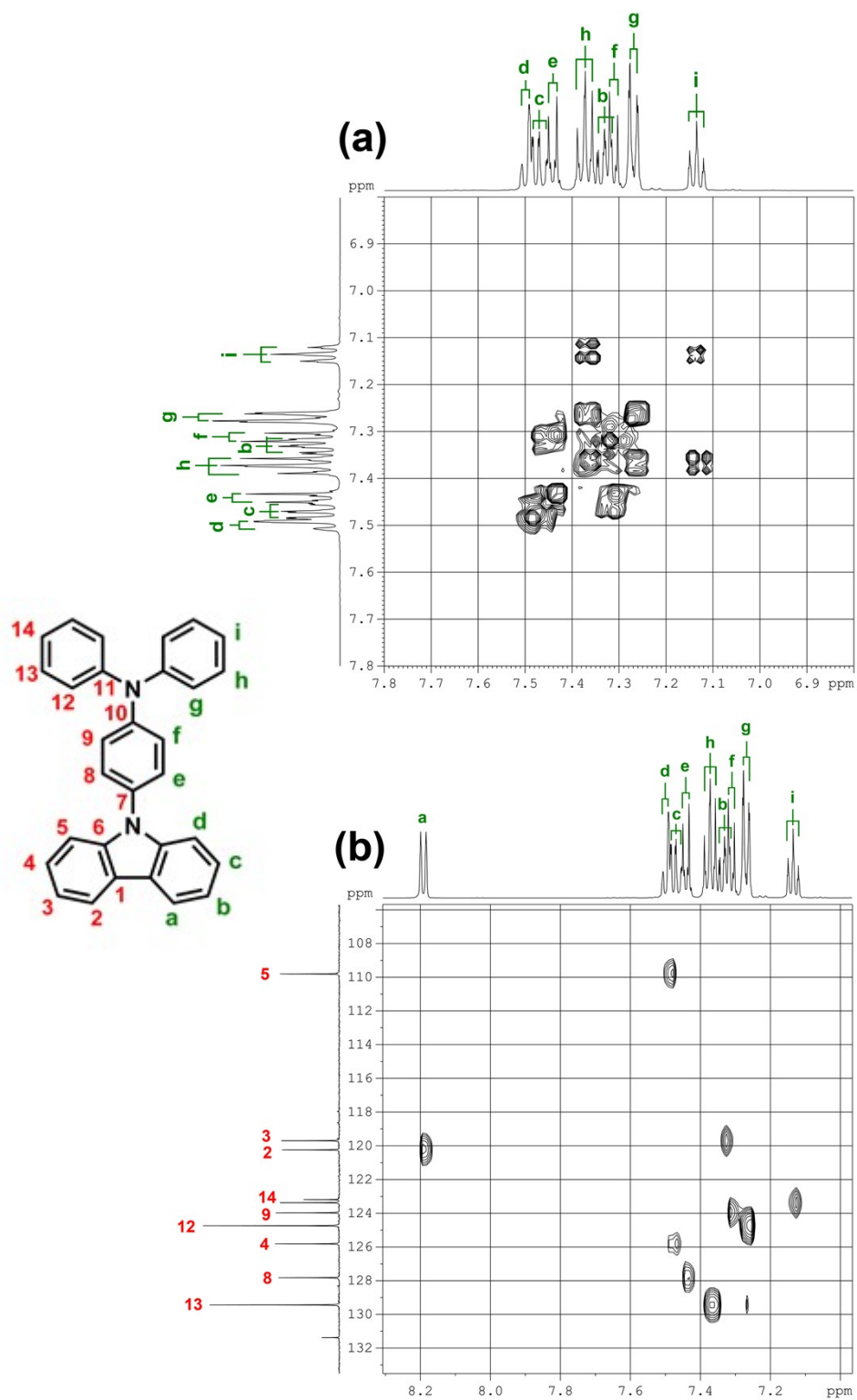


Fig. S4 (a) H-H COSY and (b) C-H HMQC spectra of TPACz in DMSO- d_6 .

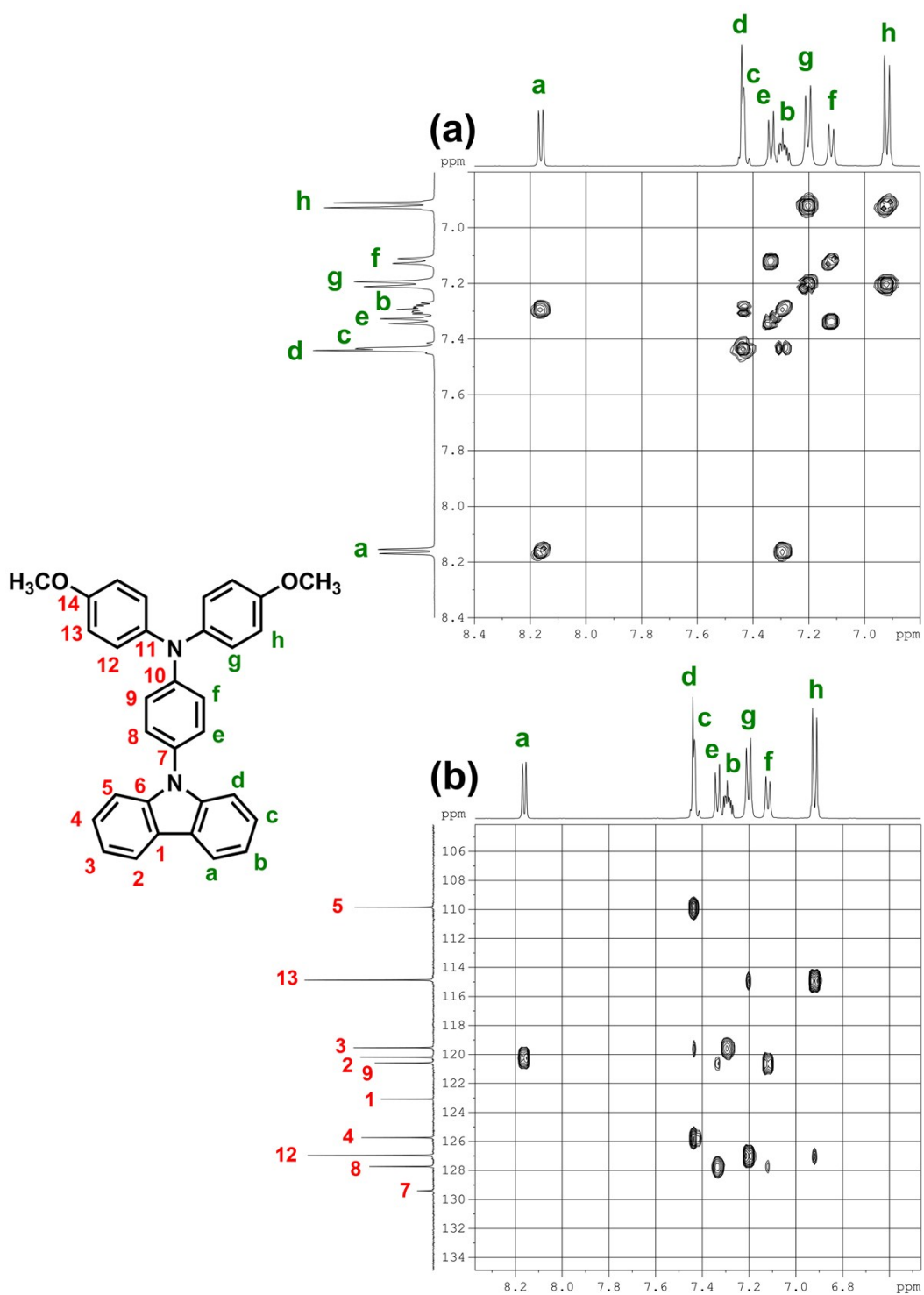


Fig. S5 (a) H-H COSY and (b) C-H HMQC spectra of MeOTPACz in DMSO- d_6 .

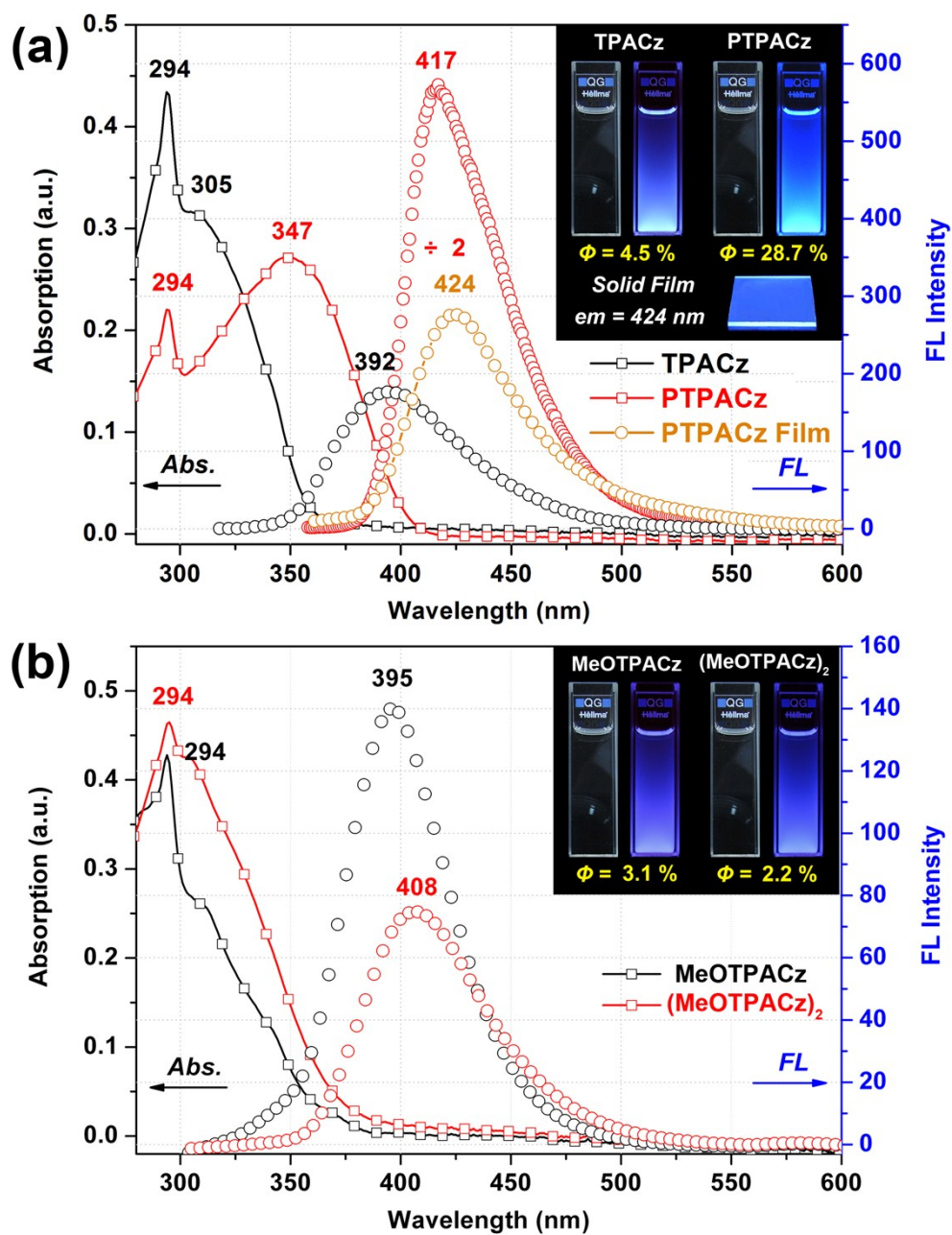


Fig. S6 UV-Vis absorption and PL spectra of the dilute solutions of (a) **TPACz** and **PTPACz** (b) **MeOTPACz** and **(MeOTPACz)₂** in CH_2Cl_2 (1×10^{-5} M). Quinine sulfate dissolved in 1 M H_2SO_4 (aq.) with a concentration of 1×10^{-5} M as the standard ($\Phi_F = 54.6\%$). Photos show PL images of the solutions upon UV exposure (excited at 365 nm).

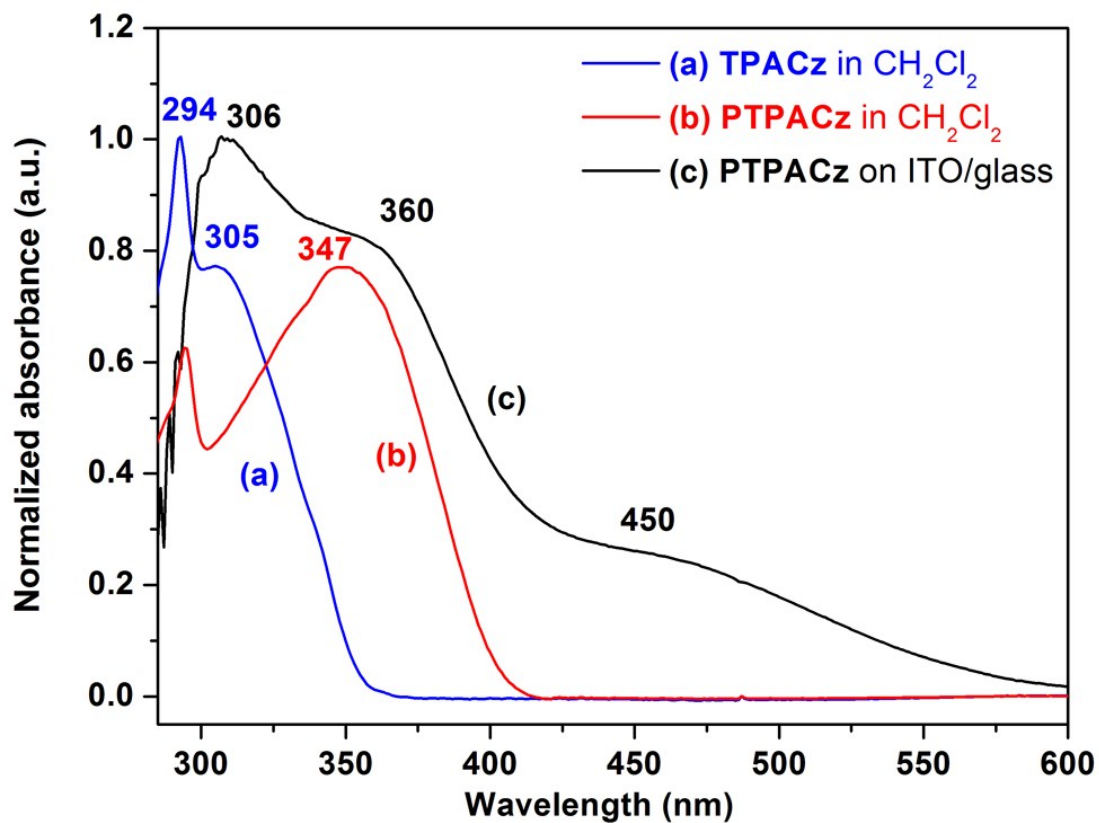


Fig. S7 UV-vis spectra of (a) TPACz monomer and (b) PTPACz in CHCl₂ solution, and (c) PTPACz on the ITO/glass surface.

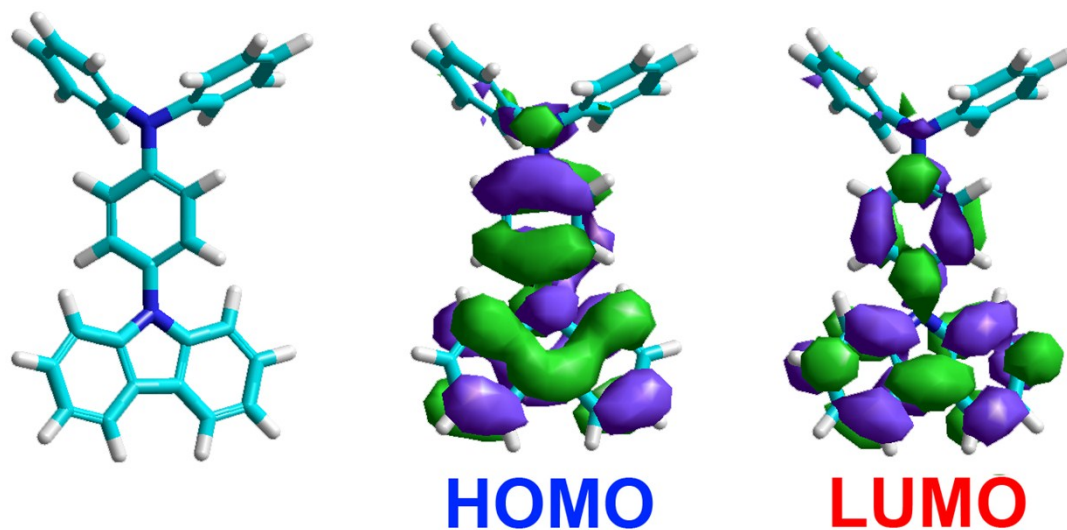
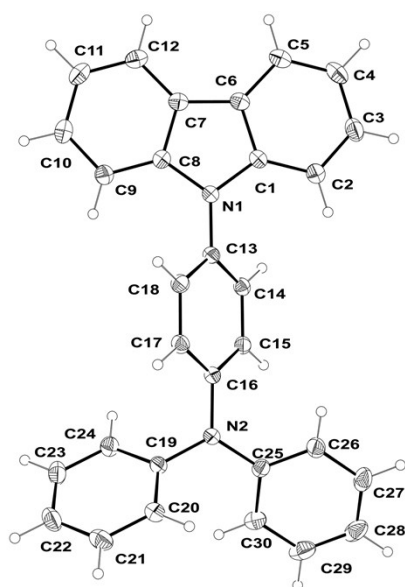
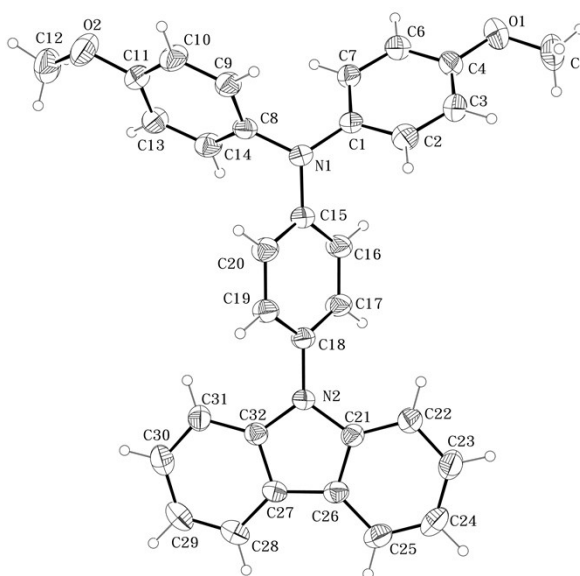


Fig. S8 Optimized geometry and spatial distributions of the HOMO and LUMO for TPACz.

Table S1 Bond lengths [\AA] and bond angles [$^\circ$] for **TPACz** and **MeOTPACz**



TPACz



MeOTPACz

TPACz			
Bond lengths [\AA]		Bond angles [$^\circ$]	
C(1)-C(2)	1.3925(19)	C(2)-C(1)-N(1)	129.62(12)
C(1)-N(1)	1.3965(17)	C(2)-C(1)-C(6)	121.64(13)
C(1)-C(6)	1.4118(18)	(1)-C(1)-C(6)	108.71(12)
C(2)-C(3)	1.382(2)	C(3)-C(2)-C(1)	117.66(14)
C(2)-H(2)	0.95	C(3)-C(2)-H(2)	121.2
C(3)-C(4)	1.393(2)	C(1)-C(2)-H(2)	121.2
C(3)-H(3)	0.95	C(2)-C(3)-C(4)	121.52(15)
C(4)-C(5)	1.378(2)	C(2)-C(3)-H(3)	119.2
C(4)-H(4)	0.95	C(4)-C(3)-H(3)	119.2
C(5)-C(6)	1.3960(19)	C(5)-C(4)-C(3)	120.74(14)
C(5)-H(5)	0.95	C(5)-C(4)-H(4)	119.6
C(6)-C(7)	1.4421(19)	C(3)-C(4)-H(4)	119.6
C(7)-C(12)	1.3988(19)	C(4)-C(5)-C(6)	119.39(14)
C(7)-C(8)	1.4041(18)	C(4)-C(5)-H(5)	120.3
C(8)-C(9)	1.3903(19)	C(6)-C(5)-H(5)	120.3
C(8)-N(1)	1.4012(16)	C(5)-C(6)-C(1)	119.03(13)
C(9)-C(10)	1.3810(19)	C(5)-C(6)-C(7)	133.84(13)
C(9)-H(9)	0.95	C(1)-C(6)-C(7)	107.12(12)
C(10)-C(11)	1.393(2)	C(12)-C(7)-C(8)	119.21(13)

C(10)-H(10)	0.95	C(12)-C(7)-C(6)	133.86(13)
C(11)-C(12)	1.372(2)	C(8)-C(7)-C(6)	106.91(11)
C(11)-H(11)	0.95	C(9)-C(8)-N(1)	129.28(12)
C(12)-H(12)	0.95	C(9)-C(8)-C(7)	121.59(12)
C(13)-C(18)	1.3866(18)	N(1)-C(8)-C(7)	109.07(11)
C(13)-C(14)	1.3894(18)	C(10)-C(9)-C(8)	117.67(13)
C(13)-N(1)	1.4231(16)	C(10)-C(9)-H(9)	121.2
C(14)-C(15)	1.3852(17)	C(8)-C(9)-H(9)	121.2
C(14)-H(14)	0.95	C(9)-C(10)-C(11)	121.56(14)
C(15)-C(16)	1.3897(18)	C(9)-C(10)-H(10)	119.2
C(15)-H(15)	0.95	C(11)-C(10)-H(10)	119.2
C(16)-C(17)	1.3913(18)	C(12)-C(11)-C(10)	120.64(13)
C(16)-N(2)	1.4222(16)	C(12)-C(11)-H(11)	119.7
C(17)-C(18)	1.3845(18)	C(10)-C(11)-H(11)	119.7
C(17)-H(17)	0.95	C(11)-C(12)-C(7)	119.31(14)
C(18)-H(18)	0.95	C(11)-C(12)-H(12)	120.3
C(19)-C(24)	1.3866(19)	C(7)-C(12)-H(12)	120.3
C(19)-C(20)	1.3892(19)	C(18)-C(13)-C(14)	119.19(12)
C(19)-N(2)	1.4270(17)	C(18)-C(13)-N(1)	120.24(12)
C(20)-C(21)	1.380(2)	C(14)-C(13)-N(1)	120.57(12)
C(20)-H(20)	0.95	C(15)-C(14)-C(13)	120.62(12)
C(21)-C(22)	1.383(2)	C(15)-C(14)-H(14)	119.7
C(21)-H(21)	0.95	C(13)-C(14)-H(14)	119.7
C(22)-C(23)	1.379(2)	C(14)-C(15)-C(16)	120.43(12)
C(22)-H(22)	0.95	C(14)-C(15)-H(15)	119.8
C(23)-C(24)	1.382(2)	C(16)-C(15)-H(15)	119.8
C(23)-H(23)	0.95	C(15)-C(16)-C(17)	118.64(12)
C(24)-H(24)	0.95	C(15)-C(16)-N(2)	121.51(12)
C(25)-C(30)	1.3910(19)	C(17)-C(16)-N(2)	119.84(12)
C(25)-C(26)	1.3920(19)	C(18)-C(17)-C(16)	121.03(12)
C(25)-N(2)	1.4141(16)	C(18)-C(17)-H(17)	119.5
C(26)-C(27)	1.386(2)	C(16)-C(17)-H(17)	119.5
C(26)-H(26)	0.95	C(17)-C(18)-C(13)	120.08(12)
C(27)-C(28)	1.376(3)	C(17)-(18)-H(18)	120
C(27)-H(27)	0.95	C(13)-C(18)-H(18)	120
C(28)-C(29)	1.369(2)	C(24)-C(19)-C(20)	119.37(13)
C(28)-H(28)	0.95	C(24)-C(19)-N(2)	119.97(13)

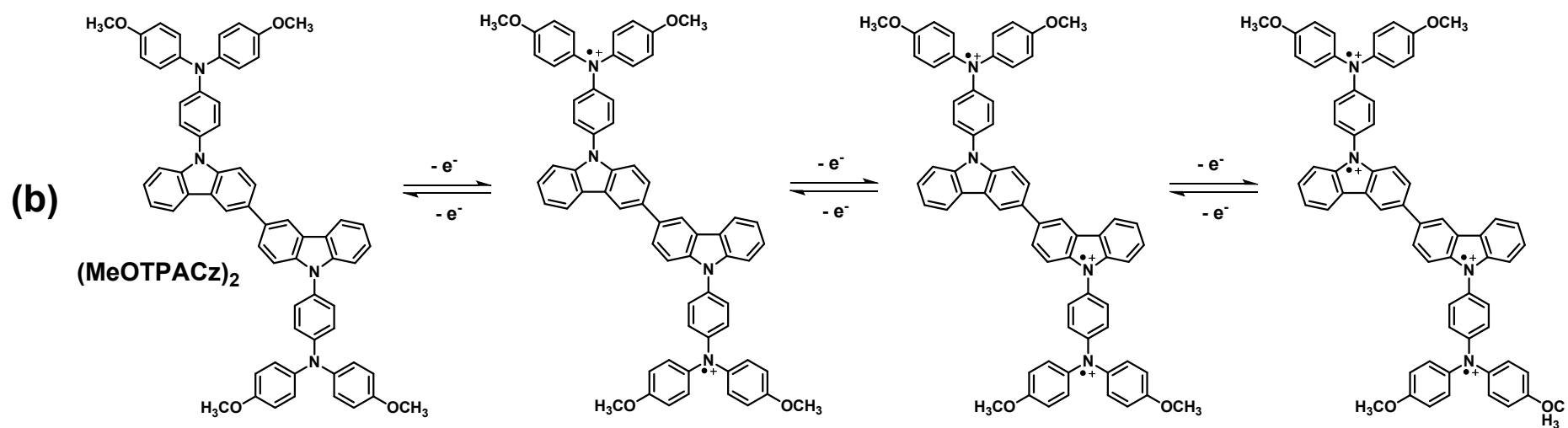
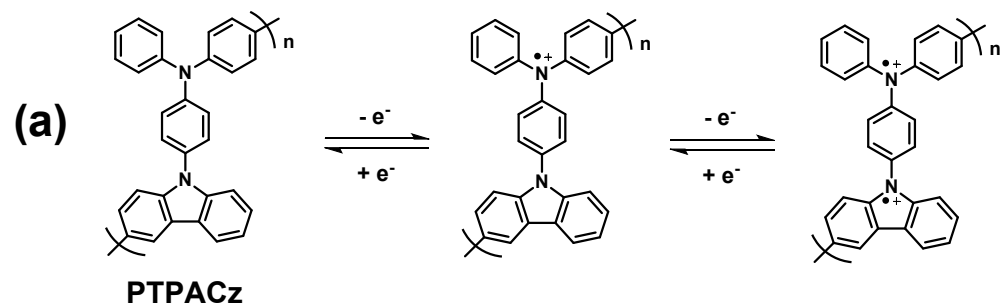
C(29)-C(30)	1.380(2)	C(20)-C(19)-N(2)	120.66(13)
C(29)-H(29)	0.95	C(21)-C(20)-C(19)	119.94(14)
C(30)-H(30)	0.95	C(21)-C(20)-H(20)	120
		C(19)-C(20)-H(20)	120
		C(20)-C(21)-C(22)	120.53(15)
		C(20)-C(21)-H(21)	119.7
		C(22)-C(21)-H(21)	119.7
		C(23)-C(22)-C(21)	119.61(15)
		C(23)-C(22)-H(22)	120.2
		C(21)-C(22)-H(22)	120.2
		C(22)-C(23)-C(24)	120.23(15)
		C(22)-C(23)-H(23)	119.9
		C(24)-C(23)-H(23)	119.9
		C(23)-C(24)-C(19)	120.30(14)
		C(23)-C(24)-H(24)	119.8
		C(19)-C(24)-H(24)	119.8
		C(30)-C(25)-C(26)	118.61(13)
		C(30)-C(25)-N(2)	120.34(13)
		C(26)-C(25)-N(2)	121.05(12)
		C(27)-C(26)-C(25)	119.92(15)
		C(27)-C(26)-H(26)	120
		C(25)-C(26)-H(26)	120
		C(28)-C(27)-C(26)	120.95(16)
		C(28)-C(27)-H(27)	119.5
		C(26)-C(27)-H(27)	119.5
		C(29)-C(28)-C(27)	119.17(15)
		C(29)-C(28)-H(28)	120.4
		C(27)-C(28)-H(28)	120.4
		C(28)-C(29)-C(30)	120.94(16)
		C(28)-C(29)-H(29)	119.5
		C(30)-C(29)-H(29)	119.5
		C(29)-C(30)-C(25)	120.40(15)
		C(29)-C(30)-H(30)	119.8
		C(25)-C(30)-H(30)	119.8
		C(1)-N(1)-C(8)	108.19(10)
		C(1)-N(1)-C(13)	125.76(11)
		C(8)-N(1)-C(13)	126.05(11)

		C(25)-N(2)-C(16)	121.29(11)
		C(25)-N(2)-C(19)	120.53(10)
		C(16)-N(2)-C(19)	118.07(10)
MeOTPAz			
Bond lengths [Å]		Bond angles [°]	
C(1)-C(7)	1.381(5)	C(7)-C(1)-C(2)	117.5(3)
C(1)-C(2)	1.385(5)	C(7)-C(1)-N(1)	122.4(3)
C(1)-N(1)	1.418(4)	C(2)-C(1)-N(1)	120.1(3)
C(2)-C(3)	1.382(5)	C(3)-C(2)-C(1)	121.5(4)
C(2)-H(2)	0.93	C(3)-C(2)-H(2)	119.2
C(3)-C(4)	1.372(5)	C(1)-C(2)-H(2)	119.2
C(3)-H(3)	0.93	C(4)-C(3)-C(2)	120.0(3)
C(4)-C(6)	1.374(5)	C(4)-C(3)-H(3)	120
C(4)-O(1)	1.378(4)	C(2)-C(3)-H(3)	120
C(5)-O(1)	1.415(5)	C(3)-C(4)-C(6)	118.9(3)
C(5)-H(5A)	0.96	C(3)-C(4)-O(1)	125.1(3)
C(5)-H(5B)	0.96	C(6)-C(4)-O(1)	116.1(3)
C(5)-H(5C)	0.96	O(1)-C(5)-H(5A)	109.5
C(6)-C(7)	1.376(5)	O(1)-C(5)-H(5B)	109.5
C(6)-H(6)	0.93	H(5A)-C(5)-H(5B)	109.5
C(7)-H(7)	0.93	O(1)-C(5)-H(5C)	109.5
C(8)-C(14)	1.372(5)	H(5A)-C(5)-H(5C)	109.5
C(8)-C(9)	1.376(5)	H(5B)-C(5)-H(5C)	109.5
C(8)-N(1)	1.432(4)	C(4)-C(6)-C(7)	121.1(3)
C(9)-C(10)	1.376(5)	C(4)-C(6)-H(6)	119.4
C(9)-H(9)	0.93	C(7)-C(6)-H(6)	119.4
C(10)-C(11)	1.381(5)	C(1)-C(7)-C(6)	120.8(3)
C(10)-H(10)	0.93	C(1)-C(7)-H(7)	119.6
C(11)-O(2)	1.373(4)	C(6)-C(7)-H(7)	119.6
C(11)-C(13)	1.373(5)	C(14)-C(8)-C(9)	119.4(3)
C(12)-O(2)	1.396(5)	C(14)-C(8)-N(1)	120.9(3)
C(12)-H(12A)	0.96	C(9)-C(8)-N(1)	119.7(3)
C(12)-H(12B)	0.96	C(8)-C(9)-C(10)	120.1(3)
C(12)-H(12C)	0.96	C(8)-C(9)-H(9)	120
C(13)-C(14)	1.379(5)	C(10)-C(9)-H(9)	120
C(13)-H(13)	0.93	C(11)-C(10)-C(9)	120.1(3)
C(14)-H(14)	0.93	C(11)-C(10)-H(10)	119.9

C(15)-C(20)	1.378(5)	C(9)-C(10)-H(10)	119.9
C(15)-N(1)	1.421(4)	C(10)-C(11)-O(2)	115.6(3)
C(15)-C(16)	1.382(5)	C(10)-C(11)-C(13)	120.1(3)
C(16)-C(17)	1.378(5)	O(2)-C(11)-C(13)	124.3(3)
C(16)-H(16)	0.93	O(2)-C(12)-H(12A)	109.5
C(17)-C(18)	1.375(5)	O(2)-C(12)-H(12B)	109.5
C(17)-H(17)	0.93	H(12A)-C(12)-H(12B)	109.5
C(18)-C(19)	1.380(4)	O(2)-C(12)-H(12C)	109.5
C(18)-N(2)	1.425(3)	H(12A)-C(12)-H(12C)	109.5
C(19)-C(20)	1.386(4)	H(12B)-C(12)-H(12C)	109.5
C(19)-H(19)	0.93	C(14)-C(13)-C(11)	119.3(3)
C(20)-H(20)	0.93	C(14)-C(13)-H(13)	120.4
C(21)-C(26)	1.392(4)	C(11)-C(13)-H(13)	120.4
C(21)-N(2)	1.398(4)	C(8)-C(14)-C(13)	121.0(3)
C(21)-C(22)	1.381(5)	C(8)-C(14)-H(14)	119.5
C(22)-C(23)	1.371(5)	C(13)-C(14)-H(14)	119.5
C(22)-H(22)	0.93	C(20)-C(15)-N(1)	119.2(3)
C(23)-C(24)	1.382(6)	C(20)-C(15)-C(16)	118.7(3)
C(23)-H(23)	0.93	N(1)-C(15)-C(16)	122.0(3)
C(24)-C(25)	1.363(6)	C(17)-C(16)-C(15)	120.7(3)
C(24)-H(24)	0.93	C(17)-C(16)-H(16)	119.7
C(25)-C(26)	1.397(5)	C(15)-C(16)-H(16)	119.7
C(25)-H(25)	0.93	C(16)-C(17)-C(18)	120.4(3)
C(26)-C(27)	1.441(4)	C(16)-C(17)-H(17)	119.8
C(27)-C(28)	1.393(4)	C(18)-C(17)-H(17)	119.8
C(27)-C(32)	1.412(4)	C(19)-C(18)-C(17)	119.5(3)
C(28)-C(29)	1.367(6)	C(19)-C(18)-N(2)	120.1(3)
C(28)-H(28)	0.93	C(17)-C(18)-N(2)	120.4(3)
C(29)-C(30)	1.386(6)	C(18)-C(19)-C(20)	119.9(3)
C(29)-H(29)	0.93	C(18)-C(19)-H(19)	120.1
C(30)-C(31)	1.370(5)	C(20)-C(19)-H(19)	120.1
C(30)-H(30)	0.93	C(15)-C(20)-C(19)	120.8(3)
C(31)-C(32)	1.384(4)	C(15)-C(20)-H(20)	119.6
C(31)-H(31)	0.93	C(19)-C(20)-H(20)	119.6
C(32)-N(2)	1.387(4)	C(26)-C(21)-N(2)	109.0(3)
		C(26)-C(21)-C(22)	122.2(3)
		N(2)-C(21)-C(22)	128.8(3)

		C(23)-C(22)-C(21)	117.3(3)
		C(23)-C(22)-H(22)	121.4
		C(21)-C(22)-H(22)	121.4
		C(22)-C(23)-C(24)	121.3(4)
		C(22)-C(23)-H(23)	119.3
		C(24)-C(23)-H(23)	119.3
		C(25)-C(24)-C(23)	121.5(3)
		C(25)-C(24)-H(24)	119.2
		C(23)-C(24)-H(24)	119.2
		C(24)-C(25)-C(26)	118.5(3)
		C(24)-C(25)-H(25)	120.7
		C(26)-C(25)-H(25)	120.7
		C(21)-C(26)-C(25)	119.1(3)
		C(21)-C(26)-C(27)	107.3(3)
		C(25)-C(26)-C(27)	133.6(3)
		C(28)-C(27)-C(32)	118.8(3)
		C(28)-C(27)-C(26)	134.6(3)
		C(32)-C(27)-C(26)	106.5(3)
		C(29)-C(28)-C(27)	119.3(4)
		C(29)-C(28)-H(28)	120.4
		C(27)-C(28)-H(28)	120.4
		C(30)-C(29)-C(28)	120.9(3)
		C(30)-C(29)-H(29)	119.6
		C(28)-C(29)-H(29)	119.6
		C(29)-C(30)-C(31)	121.8(4)
		C(29)-C(30)-H(30)	119.1
		C(31)-C(30)-H(30)	119.1
		C(32)-C(31)-C(30)	117.6(3)
		C(32)-C(31)-H(31)	121.2
		C(30)-C(31)-H(31)	121.2
		N(2)-C(32)-C(31)	129.5(3)
		N(2)-C(32)-C(27)	108.9(3)
		C(31)-C(32)-C(27)	121.6(3)
		C(15)-N(1)-C(1)	120.7(2)
		C(15)-N(1)-C(8)	117.1(2)
		C(1)-N(1)-C(8)	119.0(2)
		C(21)-N(2)-C(32)	108.3(2)

		C(21)-N(2)-C(18)	125.7(2)
		C(32)-N(2)-C(18)	125.8(2)
		C(4)-O(1)-C(5)	117.2(4)
		C(11)-O(2)-C(12)	119.2(3)



Scheme S1 Anodic oxidation pathways of (a) PTPACz and (b) (MeOTPACz)₂.