SUPPLEMENTARY INFORMATION

Electro-optical π-radicals: design advances, applications and future perspectives

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Table S1 Optical and electrochemical redox properties of π-radicals. The structures correspond to those shown in the main manuscript (additional structures are shown in Scheme S1 and S2).

Radical	λ_{peak} (nm)[a]	ε (M^{-1} cm^{-1})[b]	λ_{em} (nm)[c]	ϕ_{em} (%)[d]	τ (ns)[e]	$t_{1/2}$ (s)[f]	E_{ox} (V)[g]	E_{red} (V)[h]	Ref.	Notes
TTM	542[i] 540[ii]	690[ii]	570[i] 565[ii]	2.0[i] 0.8[ii] 76[iii]	7.0[i] 6.5[ii]	224[i] 57[ii]	+1.08[iv] +0.80[i, v]	–0.83[iv] –0.99[i, v]	1-4	[i] CH_2Cl_2; [ii] Cy; [iii] EPA, 77 K; [iv] Ag/Ag^+, CH_2Cl_2/DMF; [v] Fc/Fc^+.
PTM	564[i] 565[ii]	760[i] 910[ii]	605[i] 604[ii]	1.5[i] 1.6[ii]	7[i] 6.1[ii]	47[ii]	+1.57[iii]	–0.46[iii]	2,4,5	[i] CCl_4; [ii] Cy; [iii] Ag/Ag^+, CH_2Cl_2/DMF.
3I-PTM	400[i]	--	611[i]	91[i]	69[i]	3.2×10^{7} [i, ii] 396[iii]	--	–0.34[iv]	6	[i] solid, ≤0.01% in αH-3I-PTM; [ii] extrapolated; [iii] THF; [iv] Fc/Fc^+, THF.
PyBTM	541[i]	1 010[i]	585[i] 674[ii] 563[ii, iii]	2.2[i] 81[iv]	6.4[i] 19[ii, v] 24[ii, iii, v]	1.3×10^{4} [i]	+1.04[i, vi]	–0.74[i, vi]	1,7,8	[i] CH_2Cl_2; [ii] solid, 10% in αH-PyBTM, 4.2 K; [iii] 14.5 T; [iv] EPA, 77 K; [v] at 563 nm; [vi] Fc/Fc^+.
$[(C_6F_5)_3BN$-PyBTM]	575[i]	--	660[i]	3[i]	5.5[i]	--	--	–0.14[i, ii]	7	[i] CH_2Cl_2; [ii] Fc/Fc^+.
bisPyTM	536[i]	≤1 000[ii]	650[i] 712[iii]	0.9[i]	3.6[i]	6.7×10^{3} [i]	--	–0.57[i, iv]	3	[i] CH_2Cl_2; [ii] estimated from graph; [iii] solid, 77 K; [iv] Fc/Fc^+.
trisPyM	518[i]	933[i]	700[i] 665[ii]	0.9[i] 3.4[ii]	3.0[i] 20.0[ii]	2.2×10^{4} [i]	--	–0.42[i, iii]	9	[i] CH_2Cl_2; [ii] solid, 79 K; [iii] Fc/Fc^+.
trisZn	--	--	695[i]	2.0[i]	6.6[i] 9.3[ii] 8.9[ii, iii]	--	--	--	9,10	[i] solid, 79 K; [ii] solid, 4.2 K; [iii] 15 T.
bisZn	--	--	--[i] 626[ii, iii]	<0.1[i]	--[i] 0.4[ii] 3.5[ii, iii]	--	--	--	10	[i] solid, 79 K; [ii] solid, 4.2 K; [iii] 15 T.
D–A type										
CzBTM	554[i]	3 060[i]	697[i]	2.0[i] 5.0[ii]	4.0[i]	8.6×10^{3} [i]	–0.06[iii] –0.09[iv]	–0.92[iii] –1.03[iv]	11,12	[i] Cy; [ii] solid, 5% in CBP; [iii] Fc/Fc^+, DMF; [iv] Ag/Ag^+, CH_2Cl_2.
PyID-BTM	550[i]	5 290[i]	664[i]	19.5[i] 13.7[ii]	12.8[i]	4.0×10^{3} [i]	+0.03[iii]	–1.09[iii]	12	[i] Cy; [ii] solid, 2.5% in CBP; [iii] Ag/Ag^+, CH_2Cl_2.
TTM-1Cz	603[i] 600[ii]	3 780[i]	628[i] 687[ii]	53[i] 5[ii]	41.3[i] 13.2[ii]	--	+0.57[iii]	–0.98[iii]	13-15	[i] Cy; [ii] $CHCl_3$; [iii] Fc/Fc^+ (–0.46 V, SCE), CH_2Cl_2.
TTM-2Cz	609[i] 607[ii]	5 130[i]	680[i] 651[ii]	10[i] 54[ii]	--	--	+0.50[iii]	–0.99[iii]	16	[i] $CHCl_3$; [ii] Cy [iii] Fc/Fc^+ (–0.46 V, SCE), CH_2Cl_2.
TTM-3Cz	614[i] 611[ii]	7 000[i]	680[i] 654[ii]	7[i] 52[ii]	--	--	+0.44[iii]	–0.98[iii]	16	[i] $CHCl_3$; [ii] Cy [iii] Fc/Fc^+ (–0.46 V, SCE), CH_2Cl_2.
TTM-1BiCz	601[i]	--	671[i]	17[i]	9.9[i]	6.2×10^{4} [i]	--	--	17	[i] Cy.
TTM-2BiCz	617[i]	--	681[i]	11[i]	7.1[i]	3.1×10^{4} [i]	--	--	17	[i] Cy.
TTM-TCz	612[i]	--	689[i]	26[i]	17.2[i]	8.2×10^{4} [i]	--	--	17	[i] Cy.
TTM-αPyID	575[i] 579[ii]	--	599[i] 622[ii]	63[i] 91[ii]	40.9[i] 38.8[ii]	1.2×10^{4} [ii]	+0.44[iii]	–0.97[iii]	15	[i] Cy; [ii] $CHCl_3$; [iii] Fc/Fc^+, CH_2Cl_2.
TTM-βPyID	582[i] 581[ii]	--	610[i] 637[ii]	98[i] 89[ii]	43.6[i] 36.1[ii]	7.9×10^{5} [ii]	+0.47[iii]	–0.93[iii]	15	[i] Cy; [ii] $CHCl_3$; [iii] Fc/Fc^+, CH_2Cl_2.
TTM-γPyID	585[i] 590[ii]	--	598[i] 611[ii]	37[i] 32[ii]	36.8[i] 37.6[ii]	9.5×10^{2} [ii]	+0.55[iii]	–0.92[iii]	15	[i] Cy; [ii] $CHCl_3$; [iii] Fc/Fc^+, CH_2Cl_2.
TTM-δPyID	585[i] 581[ii]	--	614[i] 643[ii]	89[i] 99[ii]	42.7[i] 35.1[ii]	9.1×10^{5} [ii]	+0.50[iii]	–0.92[iii]	15	[i] Cy; [ii] $CHCl_3$; [iii] Fc/Fc^+, CH_2Cl_2.
TTM-3PCz	593[i]	3 250[i]	664[i] 695[iii]	29[i] 46[ii] 60[iii]	15.9[i] 21.2[ii]	--	+0.43[iv]	–1.10[iv]	2,18	[i] Cy; [ii] Tol; [iii] solid, 3% in CBP; [iv] Fc/Fc^+, CH_2Cl_2.

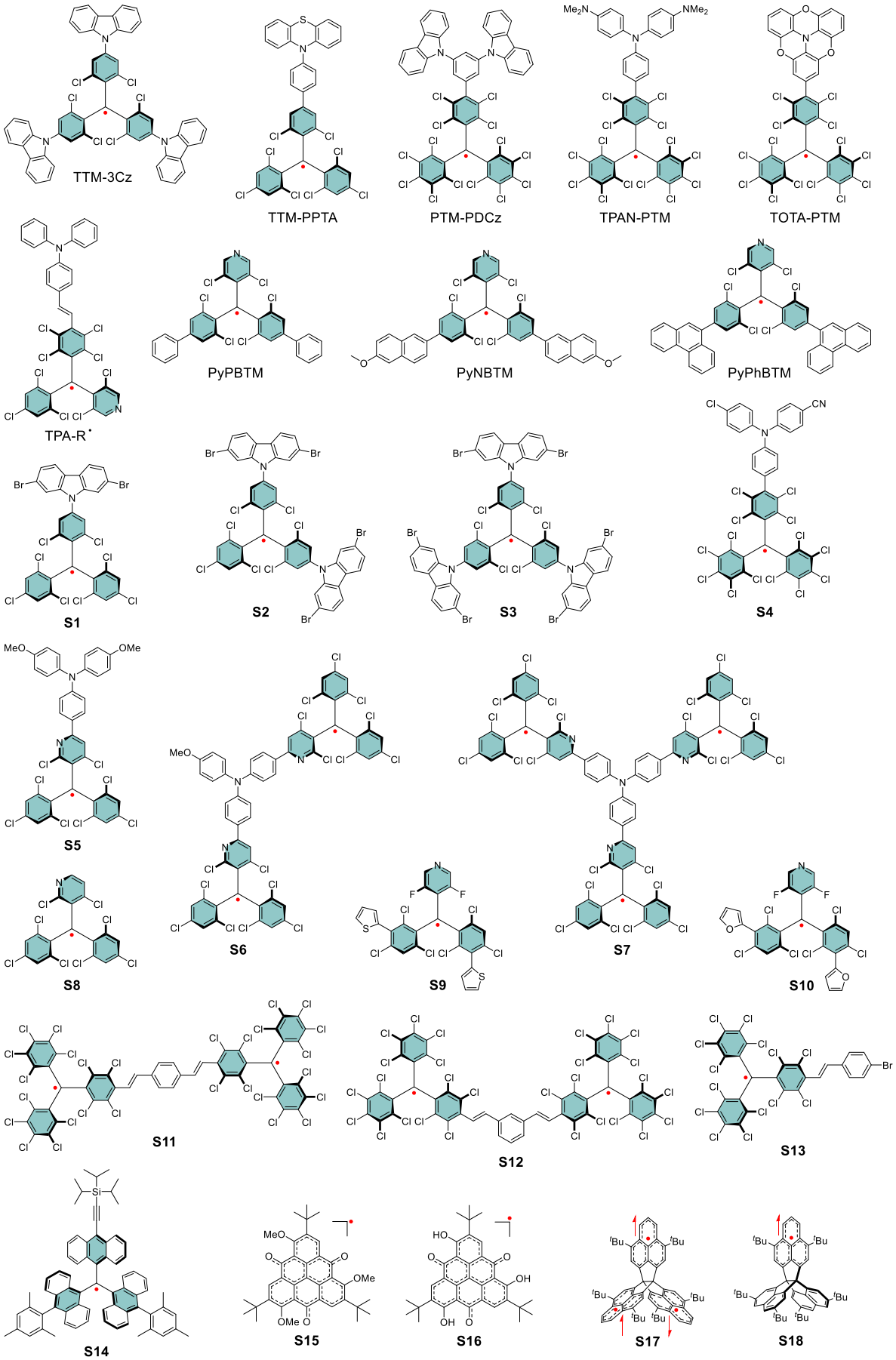
TTM-3NCz	592[i] 616[ii]	--	667[i] 707[iii]	29[i] 49[ii] 86[iii]	15.9[i] 17.2[ii]	≥1.0 × 10^4 [i, iv]	+0.71[v] +0.43[vi]	–0.86[v] –1.09[vi]	[4,18]	[i] Cy; [ii] Tol; [iii] solid, 3% in CBP; [iv] estimated from graph; [v] Ag/Ag^+, CH_2Cl_2/DMF; [vi] Fc/Fc^+, CH_2Cl_2.
TTM-PPTA	549[i]	--	775[i]	2[i]	6.8[i]	≥3.5 × 10^3 [i, ii]	+0.57[iii]	–0.84[iii]	[4]	[i] Cy; [ii] estimated from graph; [iii] Ag/Ag^+, CH_2Cl_2/DMF.
PTM-3NCz	607[i]	--	680[i]	54[i]	26.3[i]	9.1 × 10^6 [i]	+1.24[ii]	–0.58[ii]	[4]	[i] Cy; [ii] Ag/Ag^+, CH_2Cl_2/DMF.
PTM-PCz	566[i]	1 750[i]	673[i]	44[i]	26.7[i]	2.4 × 10^3 [i]	--	--	[2,4]	[i] Cy.
PTM-3PCz	606[i]	2 680[i]	679[i]	57[i]	26.3[i]	8.7 × 10^3 [i]	--	--	[2,4]	[i] Cy.
PTM-TPA	680[i]	1 960	767[i]	26[i]	15.3[i]	3.2 × 10^5 [i]	--	--	[2]	[i] Cy.
PTM-TPA″	787[i]	1 300[i]	--	--	--	--	+0.31[ii]	–0.65[ii]	[19,20]	[i] Cy; [ii] Fc/Fc^+, CH_2Cl_2.
PTM-PDCz	562[i]	--	664[i]	15[i]	142.0[i]	≥3.5 × 10^3 [i, ii]	+1.26[iii]	–0.50[iii]	[4]	[i] Cy; [ii] estimated from graph; [iii] Ag/Ag^+, CH_2Cl_2/DMF.
TPAN-PTM	973[i]	3 200[i]	--	--	--	--	–0.21[i, ii]	–0.73[i, ii]	[21]	[i] CH_2Cl_2; [ii] Fc/Fc^+.
TOTA-PTM	819[i]	1 600[i]	--	--	--	--	+0.12[i, ii]	–0.71[i, ii]	[21]	[i] CH_2Cl_2; [ii] Fc/Fc^+.
PyPBTM	567[i]	≤2 000[i, ii]	650[i] 644[iii]	8.6[i] 22[iii]	12.0[i] 21.5[iii]	1.9 × 10^4 [iv]	+0.73[iv, v]	–0.84[iv, v]	[22]	[i] $CHCl_3$; [ii] estimated from graph; [iii] EPA, 77 K; [iv] CH_2Cl_2; [v] Fc/Fc^+.
PyNBTM	618[i]	≤4 000[i, ii]	735[i] 714[iii]	6.4[i] 16[iii]	3.9[i] 7.8[iii]	2.3 × 10^4 [iv]	+0.57[iv, v]	–0.86[iv, v]	[22]	[i] $CHCl_3$; [ii] estimated from graph; [iii] EPA, 77 K; [iv] CH_2Cl_2; [v] Fc/Fc^+.
PyPhBTM	585[i]	≤2 000[i, ii]	729[i] 688[iii]	0.9[i] 7[iii]	0.8[i] 5.6[iii]	2.6 × 10^5 [iv]	+0.76[iv, v]	–0.84[iv, v]	[22]	[i] $CHCl_3$; [ii] estimated from graph; [iii] EPA, 77 K; [iv] CH_2Cl_2; [v] Fc/Fc^+.
TPA-R$^\bullet$	710[i]	1 440[i]	910[i]	0.1[i]	0.13[i]	≥9.0 × 10^2 [i, ii]	+0.38[iii]	–0.69[iii]	[23]	[i] Cy; [ii] estimated from graph; [iii] Fc/Fc^+, CH_2Cl_2.
TPA-$[RH]^{\bullet+}$	700–1400[i, ii]	--	--	--	--	--	+0.44[iii]	+0.17[iii]	[23]	[i] Cy; [ii] estimated from graph; [iii] Fc/Fc^+, CH_2Cl_2.
S1	577[i] 567[ii]	--	611[i] 594[ii]	41[i]	35.7[i]	1.7 × 10^3 [i]	--	--	[24]	[i] Tol; [ii] Cy.
S2	587[i] 577[ii]	--	629[i] 610[ii]	87[i]	33.8[i]	2.9 × 10^3 [i]	--	--	[24]	[i] Tol; [ii] Cy.
S3	592[i] 580[ii]	--	632[i] 616[ii]	84[i]	32.7[i]	5.9 × 10^3 [i]	--	--	[24]	[i] Tol; [ii] Cy.
S4	575[i]	1 300[i]	725[i]	37[i]	4.9[i]	--	--	--	[20]	[i] Cy.
S5	833[i, ii]	≤10 000[i, iii]	847[i]	2.8[i]	1.9[i]	--	+0.20[iv]	–0.95[iv]	[25]	[i] Cy; [ii] onset of absorption; [iii] estimated from graph; [iv] Fc/Fc^+, CH_2Cl_2.
S6	787[i, ii]	≥10 000[i, iii]	775[i]	6.0[i]	6.5[i]	--	+0.30[iv]	–0.94[iv]	[25]	[i] Cy; [ii] onset of absorption; [iii] estimated from graph; [iv] Fc/Fc^+, CH_2Cl_2.
S7	752[i, ii]	≤20 000[i, iii]	730[i]	6.1[i]	5.8[i]	--	+0.41[iv]	–0.89[iv]	[25]	[i] Cy; [ii] onset of absorption; [iii] estimated from graph; [iv] Fc/Fc^+, CH_2Cl_2.
S8	538[i]	682[i]	571[i] 785[iii]	1.7[i] 41[i, ii] 1.0[iii]	5.4[i] 105[i] 20.2[iii]	34[i]	--	–0.93[i, iv]	[26]	[i] CH_2Cl_2; [ii] 210 K; [iii] solid crystal; [iv] Fc/Fc^+.
S9	400–590[i, ii]	≤1 000[i, ii]	≥705[i, ii]	0.1[i] 3[iii]	0.6[i]	3.1 × 10^4 [i]	--	--	[27]	[i] Cy; [ii] estimated from graph; [iii] EPA, 77 K.
S10	400–590[i, ii]	≤1 000[i, ii]	≥675[i, ii]	0.1[i] 5[iii]	0.25[i]	6.3 × 10^3 [i]	--	--	[27]	[i] Cy; [ii] estimated from graph; [iii] EPA, 77 K.

S11	600[i]	3 200[i]	--	--	--	--	--	–0.69[i, ii]	28	[i] CH_2Cl_2; [ii] Fc/Fc^+ (–0.46 V, SCE).
S12	573[i]	3 100[i]	--	--	--	--	--	–0.69[i, ii]	28	[i] CH_2Cl_2; [ii] Fc/Fc^+.
S13	567[i]	1 500[i]	--	--	--	--	--	–0.78[i, ii]	28	[i] CH_2Cl_2; [ii] Fc/Fc^+.
Non-chlorinated										
1	1020[i]	≥200[i, ii]	--	--	--	--	–0.19[i, iii]	–1.48[i, iii]	29	[i] CH_2Cl_2, RT; [ii] estimated from graph; [iii] Fc/Fc^+.
2	395[i]	520[i]	--	--	--	--	+0.40[ii]	–1.34[ii]	30	[i] Hex, vacuum; [ii] Fc/Fc^+, CH_2Cl_2, 195 K.
BDPA	859[i]	1 580[i]	--[i, ii]	--	--	--	+0.21[i, iii]	–1.05[i, iii]	31	[i] CH_2Cl_2; [ii] RT or 77 K; [iii] Fc/Fc^+ (–0.46 V, SCE).
8	626[i]	2 720[i]	--	--	--	--	+0.27[i, ii]	–1.01[i, ii]	32	[i] CH_2Cl_2; [ii] Fc/Fc^+.
9	1220[i]	100[i]	--	--	--	--	+0.37[i, ii]	–0.90[i, ii]	33	[i] CH_2Cl_2; [ii] Fc/Fc^+.
10	669[i]	2 100[i]	--	--	--	--	+0.13[i, ii]	–1.23[i, ii]	33	[i] CH_2Cl_2; [ii] Fc/Fc^+.
11	>1000[i ii] 794[i, iii]	--[i ii] 10 000[i, iii]	--	--	--	--	+0.29[i, iv]	–0.82[i, iv]	33	[i] CH_2Cl_2; [ii] weak, estimated from graph; [iii] second-lowest energy absorption; [iv] Fc/Fc^+.
12	824[i]	≥30 000[i, ii]	--	--	--	--	+0.46[i, iii]	–0.01[i, iii] –0.24[i, iii]	34	[i] CH_2Cl_2; [ii] estimated from graph; [iii] Fc/Fc^+.
S14	1100[i]	≤300[i, ii]	--	--	--	--	–0.15[i, iii]	–1.35[i, iii]	35	[i] CH_2Cl_2, RT; [ii] estimated from graph; [iii] Fc/Fc^+.
Delocalised										
Phenalenyl	540[i, ii] 595[i, iii]	103[i, ii] 20 000[i, iii]	--	--	--	--	+0.32[iv, v]	–1.28[iv, v]	36,37	[i] CH_2Cl_2; [ii] 278 K; [iii] 191 K; [iv] Fc/Fc^+ (–0.38 V, SCE), CH_3CN; [v] E_{ox} and E_{red} were obtained from first and second reduction of cation of phenalenyl salt, respectively.
18	595i 613[ii]	--	--	--	--	--	+0.27[iii, iv]	–1.26[iii, iv]	38-40	[i] Hex, 200 K; [ii] solid, in KBr; [iii] Fc/Fc^+, CH_2Cl_2; [iv] E_{ox} and E_{red} were obtained from first and second reduction of cation of **18** salt, respectively.
19	642[i] 650[ii]	--	--	--	--	--	--	–0.30[iii, iv]	41-43	[i] Hex; [ii] solid, in KBr; [iii] Fc/Fc^+, CH_3CN; [iv] obtained from oxidation of anion of **19** salt.
21	852[i]	≥200[i, ii]	--	--	--	--	+0.56[iii, iv]	+0.09[iii, iv]	44	[i] CH_2Cl_2; [ii] estimated from graph; [iii] Fc/Fc^+, DMF; [iv] E_{red} and E_{ox} were obtained from first and second oxidation of anion of **21** salt, respectively.
TOT	834[i] 1134[ii]	≥2 000[i, iii] ≥9 000[i, iv]	--	--	--	--	+0.79[v, vi]	–0.35[v, vi]	45,46	[i] $CHCl_3$; [ii] solid, in KBr; [iii] estimated from graph, 300 K; [iv] estimated from graph, 215 K; [v] Fc/Fc^+, CH_2Cl_2; [vi] E_{red} and E_{ox} were obtained from first and second oxidation of anion of TOT salt, respectively.
22	--	--	--	--	--	--	–0.39[i, ii]	–1.42[i, ii]	47	[i] Fc/Fc^+, CH_2Cl_2; [ii] E_{ox} and E_{red} were obtained from first and second reduction of cation of **22** salt, respectively.

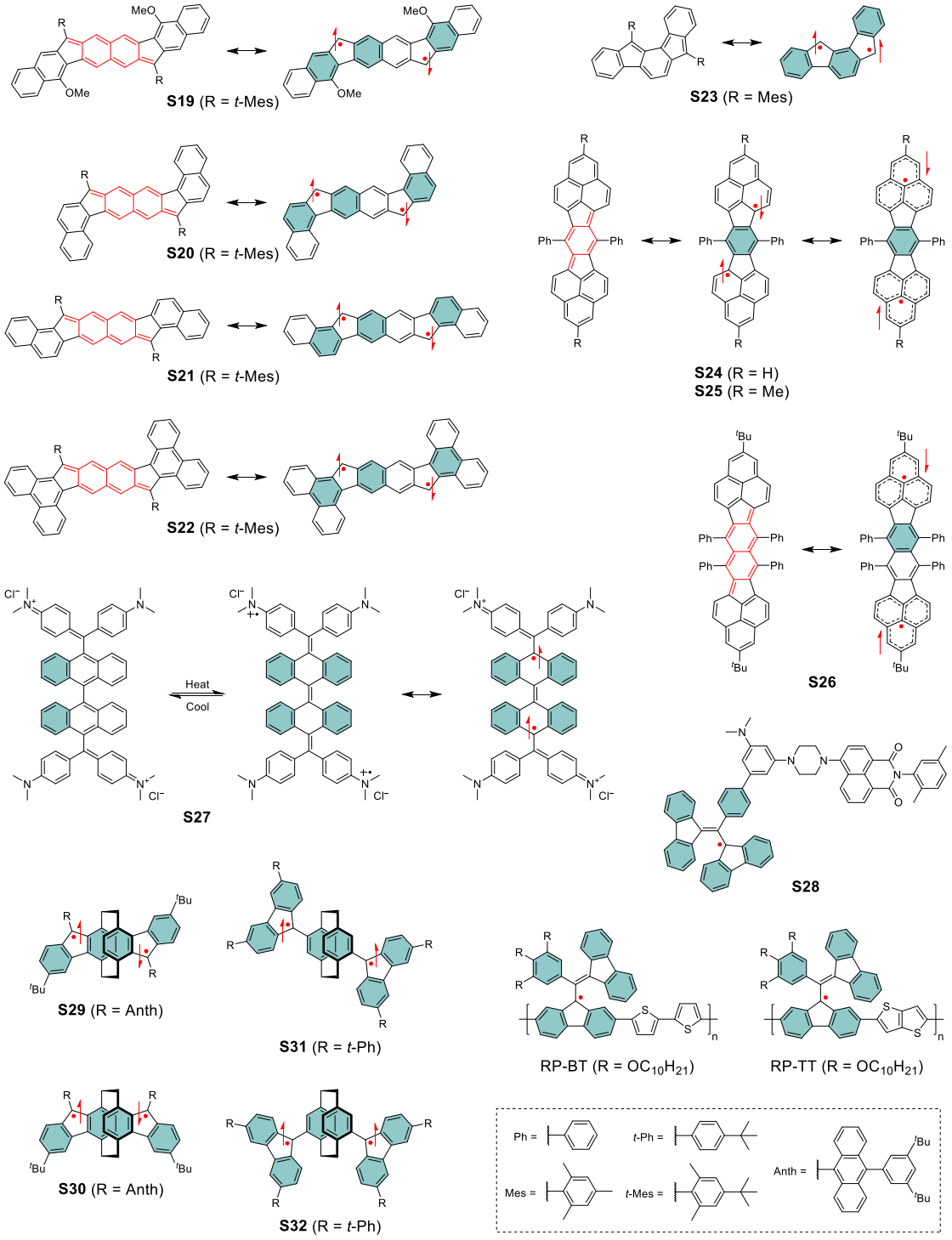
23	1355[i]	7 910[i]	--	--	--	--	--	--	47	[i] Tol.
S15	848[i] 876[ii]	--[i, iii] 9 700[i, iv]	--	--	--	--	+0.75[i, v, vi]	–0.33[i, v, vi]	46	[i] CH_2Cl_2; [ii] solid, in KBr; [iii] 300 K, no peak; [iv] 180 K; [v] Fc/Fc^+; [vi] E_{red} and E_{ox} were obtained from first and second oxidation of anion of **S12** salt, respectively.
S16	1416[i]	--	--	--	--	--	+0.74[ii, iii]	+0.03[ii, iii]	46	[i] solid, in KBr; [ii] Fc/Fc^+, CH_2Cl_2; [iii] E_{red} and E_{ox} were obtained from first and second oxidation of anion of **S13** salt, respectively.
S17	685[i]	≥4 000[ii]	--	--	--	--	–0.47[i, iii]	–1.46[i, iii]	48	[i] CH_2Cl_2; [ii] estimated from graph; [iii] Fc/Fc^+.
S18	--	--	--	--	--	--	–0.35[i]	–1.74[i]	48	[i] Fc/Fc^+, CH_2Cl_2.
Diradicals										
26	690[i,] ≤900[i, ii]	≥40 000[i, iii] --[i, ii]	--	--	--	--	+0.17[i, iv] +0.70[i, iv]	–1.28[i, iv] –1.67[i, iv]	49	[i] CH_2Cl_2; [ii] weak shoulder; [iii] estimated from graph; [iv] Fc/Fc^+.
27	537[i] 730[i, ii]	15 200[i] 790[i, ii]	--	--	--	--	+0.59[i, iii]	–1.51[i, iii]	50	[i] CH_2Cl_2; [ii] shoulder; [iii] Fc/Fc^+.
28	697[i] ≤1050[i, ii]	12 800[i] --[i, ii]	--	--	--	--	+0.38[i, iii] +0.77[i, iii]	–1.22[i, iii] –1.61[i, iii]	51	[i] CH_2Cl_2; [ii] weak shoulder; [iii] Fc/Fc^+.
29	638[i] 1700[i]	≥35 000[i, ii] ≥700[i, ii]	--	--	--	--	+0.13[i, iii] +0.90[i, iii]	–1.13[i, iii] –2.03[i, iii]	52	[i] CH_2Cl_2, RT; [ii] estimated from graph; [iii] Fc/Fc^+.
30	950[i, ii]	--	--	--	--	--	+0.33[i, iii] +0.77[i, iii]	–0.60[i, iii] –1.20[i, iii]	53	[i] CH_2Cl_2; [ii] estimated from graph; [iii] Fc/Fc^+.
31	822[i] 654[ii]	25 860[i] 15 030[ii]	--	--	--	--	+0.47[i, iii] +0.86[i, iii] +0.87[ii, iii]	–1.36[i, iii] –1.46[i, iii] –1.50[ii, iii]	54	[i] CH_2Cl_2; [ii] DMSO; [iii] Fc/Fc^+.
36	1130[i]	--[i, ii] ≥7 000[i, iii]					+0.38[i, iv] +0.52[i, iv]	–0.98[i, iv]	55	[i] CH_2Cl_2; [ii] weak, diradical; [iii] $FeCl_3$ (2 equiv.), dication of **36**; [iv] Fc/Fc^+.
37	600[i] ≤1050[i, ii]	41 000[i] --[i, ii]	--	--	--	--	+0.26[i, iii] +0.66[i, iii]	–1.13[i, iii] –1.42[i, iii]	56	[i] CH_2Cl_2; [ii] weak shoulder; [iii] Fc/Fc^+.
38	444[i, ii] 757[i, iii]	--	--	--	--	--	+0.27[i, iii, iv] +0.38[i, iii, iv] +0.94[i, ii, iv]	–0.97[i, iii, iv] –1.08[i, iii, iv] –1.74[i, ii, iv]	57	[i] CH_2Cl_2; [ii] folded form; [iii] twisted form; [iv] Fc/Fc^+.
S19	629[i]	58 900[i]	--	--	--	--	+0.17[i, ii] +0.65[i, ii]	–1.50[i, ii] –1.87[i, ii]	58	[i] CH_2Cl_2; [ii] Fc/Fc^+.
S20	688[i]	35 600[i]	--	--	--	--	+0.26[i, ii] +0.72[i, ii]	–1.28[i, ii] –1.79[i, ii]	58	[i] CH_2Cl_2; [ii] Fc/Fc^+.
S21	697[i]	50 000[i]	--	--	--	--	+0.18[i, ii] +0.65[i, ii]	–1.30[i, ii] –1.83[i, ii]	58	[i] CH_2Cl_2; [ii] Fc/Fc^+.
S22	738[i]	40 300[i]	--	--	--	--	+0.20[i, ii]	–0.75[i, ii]	58	[i] CH_2Cl_2; [ii] Fc/Fc^+.
S23	600–1000[i]	--	--	--	--	--	+0.28[ii]	–1.13[ii]	59	[i] CH_2Cl_2, estimated from graph; [ii] Fc/Fc^+ (–0.46 V, SCE), CH_2Cl_2.
S24	746[i]	178 000[i]	--	--	--	--	+0.08[i, ii]	–1.07[i, ii]	60	[i] CH_2Cl_2; [ii] Fc/Fc^+.
S25	756[i]	115 000[i]	--	--	--	--	+0.11[i, ii] +0.51[i, ii]	–1.09[i, ii] –1.62[i, ii]	61	[i] CH_2Cl_2; [ii] Fc/Fc^+.
S26	865[i]	78 430[i]	--	--	--	--	–0.13[ii] +0.26[ii]	–1.17[ii] –1.55[ii]	62	[i] Hex/CH_2Cl_2 49:1; [ii] Fc/Fc^+, CH_2Cl_2.
S27	642[i, ii] 637[i, iii]	398 000[i, ii] ≤10 000 [I, iii, iv]	699[v]	<1[v]	--	--	+0.55[v, vi]	–0.93[v, vi] –1.92[v, vi]	63	[i] DMF; [ii] 298 K; [iii] 383 K; [iv] estimated from graph; [v] CH_2Cl_2; [vi] Fc/Fc^+.

S29	660–1100[i, ii]	--[iii]	--	--	--	--	+0.11[i, iv] +0.78[i, iv]	–1.13[i, iv]	64	[i] CH_2Cl_2; [ii] estimated from graph; [iii] weak; [iv] Fc/Fc^+.
S30	660–1100[i, ii]	--[iii]	--	--	--	--	+0.09[i, iv] +0.78[i, iv]	–1.15[i, iv]	64	[i] CH_2Cl_2; [ii] estimated from graph; [iii] weak; [iv] Fc/Fc^+.
Polyradicals										
42	820[i] 794[ii] 848[iii]	6 500[i] 5 600[ii]	--	--	--	--	+0.34[ii, iv]	–0.69[ii, iv]	65	[i] Tol; [ii] CH_2Cl_2; [iii] solid film; [iv] Fc/Fc^+.
PS-CzTTM	622[i]	5 430[i]	660[i] 694[ii]	38[i] 25[ii]	19.2[i] 10.1[ii]	1.6×10^4 [i]	+0.41[iii]	–0.97[iii]	66	[i] Cy; [ii] solid film, RT; [iii] Fc/Fc^+, CH_2Cl_2.
FR-1	768[i]	800[i]	--	--	--	--	+0.12[ii]	–1.10[ii]	67	[i] Tol; [ii] Fc/Fc^+, CH_2Cl_2.
FR-2	745[i]	19 100[i]	--	--	--	--	+0.17[ii] +0.31[ii]	–1.13[ii] –1.32[ii]	67	[i] Tol; [ii] Fc/Fc^+, CH_2Cl_2.
FR-3	955[i]	11 300[i]	--	--	--	--	+0.05[ii] +0.32[ii]	–1.01[ii] –1.20[ii]	67	[i] Tol; [ii] Fc/Fc^+, CH_2Cl_2.
FR-4	735[i]	22 100[i]	--	--	--	--	+0.13[ii] +0.45[ii]	–1.09[ii] –1.30[ii]	67	[i] Tol; [ii] Fc/Fc^+, CH_2Cl_2.
FR-5	968[i]	14 200[i]	--	--	--	--	+0.00[ii] +0.16[ii]	–1.01[ii] –1.10[ii]	67	[i] Tol; [ii] Fc/Fc^+, CH_2Cl_2.
FR-6	739[i]	26 400[i]	--	--	--	--	+0.02[ii] +0.15[ii]	–1.07[ii] –1.18[ii]	67	[i] Tol; [ii] Fc/Fc^+, CH_2Cl_2.
FR-MC4	710[i] 1074[i, ii]	≤60 000[i, iii] --[i, ii]	--	--	--	--	+0.01[iv] +0.55[iv]	–1.07[iv] –1.50[iv]	68	[i] Tol; [ii] weak shoulder; [iii] estimated from graph; [iv] Fc/Fc^+, CH_2Cl_2.
FR-MC5	750[i] 966[i, ii]	≤30 000[i, iii] --[i, ii]	--	--	--	--	–0.04[iv] +0.04[iv]	–1.01[iv] –1.19[iv]	68	[i] Tol; [ii] weak shoulder; [iii] estimated from graph; [iv] Fc/Fc^+, CH_2Cl_2.
FR-MC6	772[i] 957[i, ii]	≥20 000[i, iii] --[i, ii]	--	--	--	--	+0.03[iv] +0.12[iv]	–1.07[iv] –1.23[iv]	68	[i] Tol; [ii] weak shoulder; [iii] estimated from graph; [iv] Fc/Fc^+, CH_2Cl_2.
45	1650[i]	--	--	--	--	--	–0.16[ii] –0.05[ii]	–0.99[ii] –1.05[ii]	69	[i] $CDCl_3$, weak shoulder; [ii] Fc/Fc^+, CH_2Cl_2.
RP-T	865[i]	≥2 000[i, ii]	--	--	--	--	+0.70[iii]	–0.82[iii]	70	[i] THF; [ii] estimated from graph; [iii] solid film, Fc/Fc^+, CH_3CN.
RP-BT	864[i]	≥250[i, ii]	--	--	--	--	--	--	70	[i] THF; [ii] estimated from graph.
RP-TT	857[i]	≥1 000[i, ii]	--	--	--	--	--	--	70	[i] THF; [ii] estimated from graph.

[a] Lowest-energy absorption peak wavelength. [b] Molar extinction coefficient at the peak wavelength. [c] Photoluminescence peak wavelength. [d] Photoluminescence quantum yield. [e] Luminescence lifetime. [f] Photostability (half-life of emission intensity). [g] Electrochemical oxidation potential. [h] Electrochemical reduction potential. Redox potentials are reported *vs.* ferrocene/ferrocenium (Fc/Fc^+) or Ag/Ag^+ redox couple as obtained by cyclic voltammetry and noted in the table. Up to four redox reactions are reported for diradicals and polyradicals. If potential values were referenced to standard calomel electrode (SCE), conversion values of –0.46 (V *vs.* Fc/Fc^+ in CH_2Cl_2)[71] and –0.38 (V *vs.* Fc/Fc^+ in CH_3CN)[72] were used, as noted in the table. All data have been obtained at room temperature, unless noted otherwise. Key: --, not reported; Cy, cyclohexane; Hex, hexane; Tol, toluene; EPA, diethyl ether/isopentane/ethanol 5:5:2 v/v; DMSO, dimethyl sulfoxide; DMF, *N*,*N*-dimethylformamide; THF, tetrahydrofuran; CBP, 4,4'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl.



Scheme S1 Chemical structures of additional π-radicals listed in Table S1.



Scheme S2 Chemical structures of additional π-radicals, diradicals and polyradicals listed in Table S1 (R groups are omitted from some resonance structures for clarity).

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