Supporting Information

A near-infrared luminescent organic radical with switchable

emission and SOMO-HOMO inversion via

protonation/deprotonation process

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Materials and methods

All chemicals were purchased from Tansoole Chemicals and commercial suppliers and used as received unless stated otherwise. THF and CHCl₃ were distilled with standard methods before use.

The ¹H-NMR spectra were recorded with a Bruker AVANCZ 500 spectrometer at 400 or 500 MHz, using deuterated chloroform (CDCl₃) as solvent at 298 K. The mass spectra of the radical were recorded on LCMS-IT-TOF (Shimadzu) for high resolution. Fourier transform Infrared (FT-IR) spectra were recorded using a Bruker VERTEX 70. Ultraviolet-visible (UV-vis) absorption spectra of the radicals were recorded on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra of the radicals were performed using an Agilent G9800A spectrophotometer. An Edinburgh fluorescence spectrometer (FLS1000) was used for the fluorescence decay and absolute fluorescence measurements, and the lifetime of the excited states was measured by the timecorrelated single photon counting method under the excitation of a laser (378 nm). EPR spectra were recorded on a Bruker ELEXSYS II E500 CW-EPR spectrometer at ambient temperature in dichloromethane. The CV curves of the radical measurements were performed using an electrochemical analyzer (CHI760C, CH Instruments). A glass carbon disk was used as the working electrode. A platinum wire acted as the counter electrode, and Ag/Ag⁺ acted as the reference electrode, together with the redox couple ferrocenium/ferrocene as the internal standard at the rate of 50 or 100 mV·s⁻¹. Tetrabutylammonium hexafluorophosphate $(TBAPF_6)$ in anhydrous MeCN (acetonitrile) /DCM (dichloromethane) (2/3, v/v) (0.1 M) was used as the supporting electrolyte for negative and positive scans, respectively. Column chromatography was performed with silica gel (300-400 mesh). The photostability of the radicals was achieved by measuring the decay of 375 nm-centered UV-vis spectra under 365 nm UV lamp irradiation. The DFT and TD-DFT calculations were performed on the Gaussian 09 programs using m062x and UB3LYP function and 6-31G (d, p) basis.

Synthesis and characterization of the compounds

Synthesis of intermediates 6-butyl-indolo[3,2-b]carbazole (ICz) and TTM: The radical TTM^[1] and 6-butyl-indolo[3,2-b]carbazole (ICz)^[2] were prepared according to the previous report (Scheme S1).



Scheme S1. synthetic procedure of ICz and radical TTM, TTM-EMICz

Synthesis of 6-butyl-indolo[3,2-b]carbazole (ICz): The I₂ (0.23 g, 0.9 mmol) was added to a mixture of indole (1.077 g, 9.2 mmol) and valeraldehyde (0.50 mL, 4.6 mmol) in CH₃CN. The reaction mixture was stirred at 25 °C for 14 h. After the reaction was completed, the reaction was quenched with saturated Na₂SO₃ (50 mL) aqueous solution. And extracted with ethyl acetate (EtOA) (3×30 mL), the organic layer was washed with saturated Na₂SO₃ (50 mL) aqueous solution to remove the excess I₂, then washed with distilled water several times, the organic layer was collected, and the solvent was removed under reduced pressure. The collected organic layer was dried with anhydrous Na₂SO₄. The achieved red viscous liquid was dissolved in 6 mL of methanol, and then triethyl orthoformate (0.76 mL, 4.6 mmol) and methanesulfonic

acid (60.0 µL, 0.92 mmol) were added to the reaction mixture. The reaction was stirred at 25 °C overnight. Filtered off the formed precipitate and washed with methanol several times. Finally achieved 0.41 g light yellow target product (ICz) with a yield of 28.5%. ¹H NMR (600 MHz, DMSO) δ 10.9 (d, *J* = 83.9 Hz, 2H), 8.2 (dd, *J* = 19.1, 7.8 Hz, 2H), 7.98 (s, 1H), 7.50 (t, *J* = 8.7 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.14 (dt, *J* = 27.8, 7.4 Hz, 2H), 3.57-3.43 (m, 2H), 1.88-1.73 (m, 2H), 1.67-1.53 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (151 MHz, DMSO) δ 141.69, 135.98, 134.48, 125.86, 125.20, 123.32, 122.99, 122.68, 122.30, 122.27, 120.73, 120.56, 118.66, 118.27, 118.03, 111.05, 110.84, 98.41, 31.76, 28.65, 23.06, 14.61.

Synthesis of TTM-EMICz: Under the nitrogen atmosphere, TTM (0.88 g, 1.6 mmol), ICz (0.25 g, 0.80 mmol), t-BuONa (0.077 g, 0.80 mmol), tri-tert-butylphosphonium tertrafluoroborate (TTBF) (0.042 g, 0.144 mmol), and palladium acetate (0.011 g, 0.048 mmol), were dissolved in toluene solution (30 mL), the mixture was stirred at 110 °C for 36 h in the dark. After the reaction was completed, the mixture was cooled to room temperature and extracted with dichloromethane. The crude product was adsorbed in silica gel and purified by silica gel column chromatography using (petroleum ether: dichloromethane = 6:1v/v), finally obtained a dark green solid with yields of TTM-EMICz (9%). TTM-EMICz-HRMS (m/z) Calculated for $C_{41}H_{25}Cl_8N_2$ [M+H]⁺ : 825.9599, found: 825.9424



Figure S1. The ¹H-NMR spectrum of ICz



Figure S2. The ¹³C-NMR spectrum of ICz



Figure S3. HRMS spectrum of radical TTM-EMICz



Figure S4. IR spectra of ICz and radical TTM-EMICz



Figure S5. Electron paramagnetic resonance (EPR) spectra of TTM-EMICz in CH_2Cl_2 at room temperature

Photophysical properties of radicals



Figure S6. Absorption spectra of (a) TTM-EMICz in cyclohexane solution with different concentrations; absorption intensity of (b) TTM-EMICz at 332 nm, 375 nm, and 701 nm as a function of concentration



Figure S7. Absorption spectra of the radical TTM-EMICz in different polar solvents



Figure S8. PL spectra of radicals TTM-1Cz and TTM-EMICz in cyclohexane



Figure S9. Molecular frontier orbitals of ICz, TTM, and protonated ICz (ICz-H⁺) calculated by DFT (UB3LYP/6-31G(d,p))



Figure S10. PL spectra changes of protonated radical TTM-EMICz (10⁻⁵ mol/L) (TTM-EMICz-H⁺) upon addition of TfOH into toluene, the inset shows the photograph under UV lamp irradiation.



Figure S11. Optimized ground state molecular frontier orbitals of TTM-EMICz by (cam-b3lyp/6-31g(d,p))



Figure S12. Optimized ground state molecular frontier orbitals of TTM-EMICz by (m062x/6-31g(d,p))



Figure S13. The photostability of the protonated radical TTM-EMICz (TTM-EMICz-H⁺) and TTM (measured by PL decays) in cyclohexane and toluene solution

TD-DFT calculations

TTM-EMICz (Optimized ground state structure, ub3lyp/6-31g(d,p))

Excitation energies and oscillator strengths:

1.3930 eV 890.02 nm f=0.0830 <S**2>=0.812 Excited State 1: 2.061-A 210B ->211B 0.99259 This state for optimization and/or second-order correction. Total Energy, E(TD-HF/TD-KS) = -5368.48174790 Copying the excited state density for this state as the 1-particle RhoCI density. 1.8005 eV 688.60 nm f=0.0007 <S**2>=0.813 Excited State 2: 2.062-A 209B ->211B 0.99762 2.3426 eV 529.27 nm f=0.0279 <S**2>=0.841 Excited State 3: 2.089-A 201B ->211B -0.10667 204B ->211B -0.16363 208B ->211B 0.95439 Excited State 4: 2.218-A 2.6646 eV 465.30 nm f=0.0136 <S**2>=0.980 209A ->212A 0.27582 211A ->212A -0.16336 202B ->211B -0.20383203B ->211B 0.22569 205B ->211B 0.68744 206B ->211B -0.48901 Excited State 5: 3.446-A 2.6881 eV 461.24 nm f=0.0000 <S**2>=2.718 210A ->214A 0.34536 211A ->214A 0.57383 209B ->212B -0.11324209B ->214B -0.30827210B ->212B 0.13349 210B ->214B 0.54481 210B ->220B -0.10376 Excited State 6: 2.261-A 2.7715 eV 447.35 nm f=0.0030 <S**2>=1.029 209A ->213A 0.26601 211A ->213A -0.28112 201B ->211B 0.28972 204B ->211B 0.76229 205B ->211B 0.10195

208B ->211B 0.24587

Excited State 7: 3.447-A 2.8455 eV 435.73 nm f=0.0001 <S**2>=2.721 209A ->214A -0.15274210A ->214A 0.52053 211A ->214A -0.38425 209B ->212B -0.19077209B ->214B -0.51984 210B ->212B -0.11480210B ->214B -0.32446 Excited State 8: 2.120-A 2.8743 eV 431.35 nm f=0.0030 <S**2>=0.873 209A ->212A 0.17073 211A ->212A -0.13576 202B ->211B -0.28971 203B ->211B 0.77721 205B ->211B -0.19132 206B ->211B 0.41211 Excited State 9: 2.310-A 2.9466 eV 420.77 nm f=0.0307 <S**2>=1.084 209A ->213A 0.22016 211A ->213A -0.43667 201B ->211B 0.61636 204B ->211B -0.53334 Excited State 10: 2.111-A 2.9624 eV 418.53 nm f=0.0036 <S**2>=0.864 209A ->212A -0.12627 209A ->215A 0.13118 211A ->212A 0.10186 202B ->211B 0.83538 203B ->211B 0.42934 205B ->211B 0.15431 Excited State 11: 2.699-A 3.0374 eV 408.20 nm f=0.1326 <S**2>=1.571 208A ->213A 0.10211 211A ->213A 0.59095 200B ->211B 0.32372 201B ->211B 0.57711 210B ->212B 0.20012 Excited State 12: 2.084-A 3.1757 eV 390.41 nm f=0.0074 <S**2>=0.836 200B ->211B -0.15855 207B ->211B 0.95872

Excited State 13: 2.321-A 3.2163 eV 385.48 nm f=0.0649 <S**2>=1.096 209A ->212A 0.11435 209A ->220A 0.12253 209A ->221A -0.11029211A ->212A -0.23443211A ->213A -0.28027 199B ->211B 0.12010 200B ->211B 0.70434 201B ->211B -0.24097-0.20908 205B ->211B 206B ->211B -0.16838 207B ->211B 0.17750 3.2187 eV 385.20 nm f=0.1011 <S**2>=1.071 Excited State 14: 2.299-A 209A ->212A -0.38127 211A ->212A 0.69956 211A ->213A -0.20632 200B ->211B 0.19482 202B ->211B -0.30404 203B ->211B 0.21931 205B ->211B 0.18018 3.2510 eV 381.37 nm f=0.0164 <S**2>=0.852 Excited State 15: 2.099-A 200B ->211B 0.12539 201B ->211B -0.11698 203B ->211B -0.22220204B ->211B -0.14501 205B ->211B 0.55342 206B ->211B 0.70483 207B ->211B 0.13426 210B ->212B 0.18743 3.2881 eV 377.07 nm f=0.1555 <S**2>=1.565 Excited State 16: 2.694-A 209A ->213A 0.24397 211A ->213A -0.15072211A ->214A -0.10770200B ->211B -0.20304205B ->211B -0.11895 206B ->211B -0.15036 210B ->212B 0.85190 Excited State 17: 2.705-A 3.3150 eV 374.01 nm f=0.0083 <S**2>=1.579 209A ->212A 0.13792 209A ->215A -0.26652

211A ->214A 0.18453 211A ->215A 0.71755 211A ->217A -0.47566 202B ->211B 0.11275 205B ->211B -0.10053 210B ->217B -0.12352 Excited State 18: 2.072-A 3.3647 eV 368.49 nm f=0.0265 <S**2>=0.823 211A ->214A -0.63794 211A ->215A 0.18042 210B ->214B 0.70166 Excited State 19: 3.110-A 3.4581 eV 358.53 nm f=0.0098 <S**2>=2.167 208A ->212A 0.10506 209A ->212A 0.33559 209A ->215A 0.24846 209A ->217A 0.12648 211A ->212A 0.40893 211A ->215A -0.31188 211A ->217A -0.26553 203B ->211B -0.12344 205B ->211B -0.10165 210B ->213B 0.51705 210B ->215B 0.18226 210B ->217B -0.14413 Excited State 20: 2.452-A 3.4925 eV 355.00 nm f=0.0195 <S**2>=1.253 208A ->213A 0.11245

209A ->213A

210A ->213A

211A ->213A

201B ->211B

204B ->211B 210B ->212B 0.69783

0.20587

0.37626

-0.23448 -0.16590

-0.24033

TTM-EMICz (Optimized first doublet excited state structure, ub3lyp/6-31g(d,p)) Excitation energies and oscillator strengths:

Excited State 1: 2.061-A 1.3930 eV 890.02 nm f=0.0830 <S**2>=0.812 210B ->211B 0.99259 This state for optimization and/or second-order correction. Total Energy, E(TD-HF/TD-KS) = -5368.48174791Copying the excited state density for this state as the 1-particle RhoCI density. 1.8005 eV 688.60 nm f=0.0007 <S**2>=0.813 Excited State 2: 2.062-A 209B ->211B 0.99762 Excited State 3: 2.089-A 2.3425 eV 529.27 nm f=0.0279 <S**2>=0.841 201B ->211B -0.10667 204B ->211B -0.16363 208B ->211B 0.95439 Excited State 4: 2.218-A 2.6646 eV 465.30 nm f=0.0136 <S**2>=0.980 209A ->212A 0.27583 211A ->212A -0.16336 202B ->211B -0.20383 203B ->211B 0.22569 205B ->211B 0.68744 206B ->211B -0.48901 Excited State 5: 3.446-A 2.6881 eV 461.24 nm f=0.0000 <S**2>=2.718 210A ->214A 0.34536 211A ->214A 0.57383 209B ->212B -0.11324 209B ->214B -0.30827210B ->212B 0.13349 210B ->214B 0.54482 210B ->220B -0.103762.7715 eV 447.35 nm f=0.0030 <S**2>=1.029 Excited State 6: 2.261-A 209A ->213A 0.26601 211A ->213A -0.28112201B ->211B 0.28972 204B ->211B 0.76229 205B ->211B 0.10195 208B ->211B 0.24587 2.8455 eV 435.73 nm f=0.0001 <S**2>=2.721 Excited State 7: 3.447-A

209A ->214A -0.15274

210A ->214A	0.52053
211A ->214A	-0.38425
209B ->212B	-0.19077
209B ->214B	-0.51984
210B ->212B	-0.11480
210B ->214B	-0.32446

Excited State 8: 2.120-A 2.8743 eV 431.35 nm f=0.0030 <S**2>=0.873 209A ->212A 0.17073 211A ->212A -0.13576 202B ->211B -0.28971 203B ->211B 0.77721 205B ->211B -0.19132 206B ->211B 0.41211

2.9466 eV 420.77 nm f=0.0307 <S**2>=1.084 Excited State 9: 2.310-A 209A ->213A 0.22016 211A ->213A -0.43667 201B ->211B 0.61636 204B ->211B -0.53335 2.9624 eV 418.53 nm f=0.0036 <S**2>=0.864 Excited State 10: 2.111-A 209A ->212A -0.12627 209A ->215A 0.13118 211A ->212A 0.10186

202B ->211B0.83538203B ->211B0.42934205B ->211B0.15431

TTM-EMICz+H (Optimized first doublet excited state structure, ub3lyp/6-31g(d,p))

Excitation energies and oscillator strengths:

Excited State 1: 2.176-A 2.4190 eV 512.55 nm f=0.0035 <S**2>=0.934 210A ->212A -0.11283 211A ->212A 0.98808 This state for optimization and/or second-order correction. Total Energy, E(TD-HF/TD-KS) = -5368.80698872 Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.151-A 2.5276 eV 490.52 nm f=0.0358 <S**2>=0.907 211A ->217A -0.20739 0.14507 208B ->211B 209B ->211B 0.92203 210B ->211B 0.10608 Excited State 3: 2.197-A 2.6064 eV 475.69 nm f=0.0248 <S**2>=0.956 211A ->214A 0.17762 211A ->215A -0.23197 203B ->211B -0.17381205B ->211B -0.41228 206B ->211B 0.14380 208B ->211B 0.43001 209B ->211B -0.14204210B ->211B 0.64603

2.7239 eV 455.18 nm f=0.0001 <S**2>=2.737 Excited State 4: 3.457-A 200A ->212A -0.13097 207A ->212A -0.36592 208A ->212A -0.50135 210A ->212A -0.12973200B ->212B 0.13251 207B ->211B 0.11355 207B ->212B 0.60407 208B ->212B -0.12392210B ->212B 0.13040 2.7400 eV 452.49 nm f=0.0079 <S**2>=0.876 Excited State 5: 2.122-A 211A ->215A 0.12774 205B ->211B 0.28697

206B ->211B -0.20319 207B ->211B 0.17877

208B ->211B 0.82973

209B ->211B	-0.14640				
210B ->211B	-0.22029				
Excited State 6.	2 008-1	2 8145 eV	110 53 nm	f=0.0059	<\$**2>=0.850
205B ->211B	0.17409	2.0145 CV	10.33 IIII	1-0.0037	-5 22-0.050
205B ->211B 206B ->211B	0.07407				
200B -> 211B 208B -> 211B	0.13964				
200B ->211B	0.13704				
210B ->211B	-0.10101				
.		• • • • • • • •			
Excited State 7:	3.252-A	2.8990 eV	427.68 nm	t=0.0028	<s**2>=2.393</s**2>
20/A ->212A	0.12045				
210A ->212A	-0.56324				
210A ->218A	0.11393				
211A ->212A	-0.12781				
205B ->211B	0.29333				
207B ->212B	-0.126/4				
210B ->211B	0.26154				
210B ->212B	0.59513				
Excited State 8:	2.330-A	2.9166 eV	425.09 nm	f=0.0060	<s**2>=1.108</s**2>
210A ->212A	0.19941				
211A ->213A	-0.49627				
203B ->211B	-0.17969				
205B ->211B	0.62291				
210B ->211B	0.36357				
210B ->212B	-0.20856				
Excited State 9:	2.249-A	2.9225 eV	424.24 nm	f=0.0405	<s**2>=1.015</s**2>
210A ->212A	0.17679				
211A ->213A	0.80432				
211A ->214A	-0.13864				
211A ->215A	0.13896				
205B ->211B	0.20296				
210B ->211B	0.40307				
210B ->212B	-0.18855				
Excited State 10.	2 194-a	3 0723 eV	403 55 nm	f=0.0390	<\$**7>=0 953
211A ->213A	0 15971	5.0725 € 4	40 <i>5.55</i> mm	1 0.0570	
211A ->213A	0.23682				
211A ->215A	-0 30852				
211A ->216A	-0 25807				
203R ->211R	-0 20747				
203B - 211B 204B ->211B	0 75029				
	0.75029				

205B ->211B	0.16619
207B ->211B	-0.13035
210B ->211B	-0.16037

References

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