Electronic Supplementary Information (ESI)

A conjugated porphyrin as a red light sensitizer for near-infrared emission of ytterbium (III)

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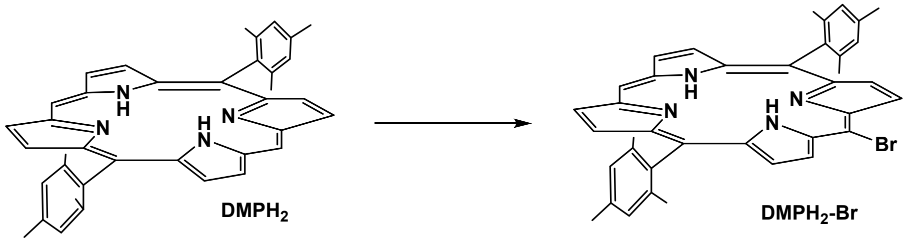
Experimental

General Comments. All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was supplied by Biosynth International, Inc. Tetrahydrofuran (THF), dimethylformamide (DMF), deuterated chloroform ($CDCl_3$), N-bromosuccinimide (NBS), copper(I) iodide (CuI), tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$), 2,4-dimethylpyrrole and mesitaldehyde were purchased from ACROS Organics. 2,2´-dipyrrolmethane was synthesized based upon a method developed by Dr. He. The 230-400 mesh silica gel was purchased from Dynamic Adsorbents, Inc. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Avance II-NMR spectrometer, using ACROS Organics chloroform-d 99.8% D, containing 0.03% (v/v) TMS as the solvent. All ^{1}H NMR signals were referenced to TMS. The chemical shifts were reported in parts per million (ppm). For the signal splitting, the following abbreviations are used: *s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet; *bs*, broad singlet. UV-Vis absorption spectra were performed on a Cary 100 Series UV-Vis Dual Beam Spectrophotometer over a range of 200 - 800 nm. 5,15-Dimesitylporphyrin ($DMPH_2$) was synthesized according a literature method[1] and its structure was confirmed by ^{1}H NMR. Glovebox was from Vacuum Technology Inc.

Synthesis of DMPH2-Br.



To a solution of 5,10-dimesitylporphyrin (228 mg, 0.418 mmol) in CH_2Cl_2 (500 mL) at an ice bath was added NBS (102 g, 0.576 mmol) in 50 mL dichloromethane dropwise within one hour. The temperature of the solution was slowly increased to room temperature. The reaction mixture was further stirred overnight. The solvent was removed under reduced pressure and the final product was purified on a column chromatography (silica gel, CH_2Cl_2: Hexane = 1:4, v/v). The second and was collected as the monobrominated product, DMPH$_2$-Br. Yield: 140 mg, 54%. ^{1}H NMR (400MHz, $CDCl_3$) δ 10.07 (*s*, 1 H, ^{a}H), 9.645 (*d*, 2H, ^{b}H), 9.21(*d*, 2H, ^{c}H), 2.55 (s, 6H), 1.37(s,6H), -2.87 (s, 2H).

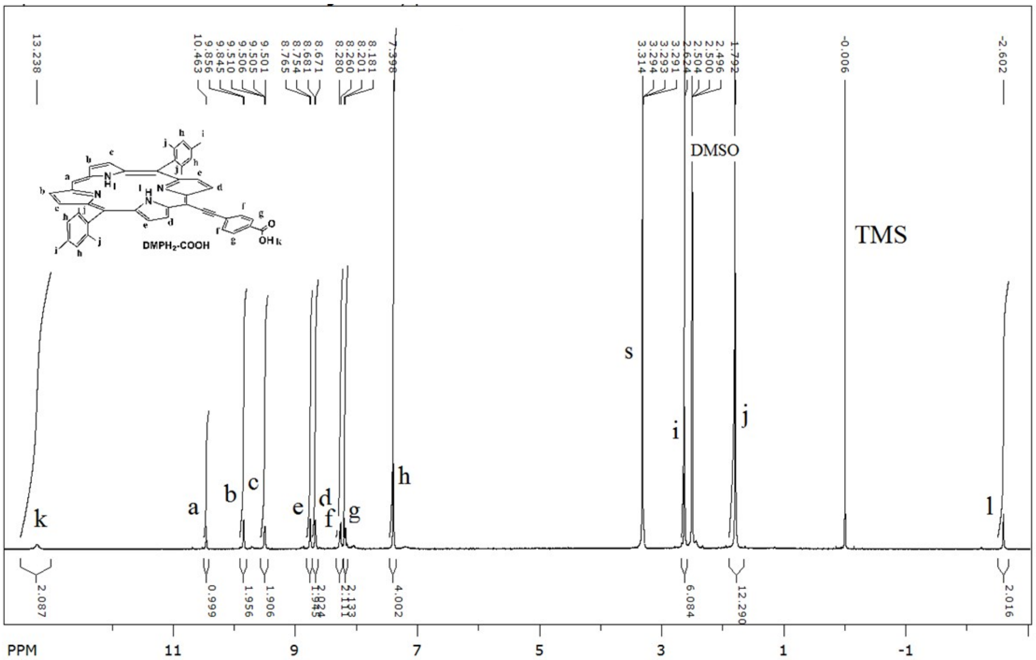


Fig. S1 ^{1}H NMR spectrum of DMPH$_2$-COOH in DMSO-d_6. S stands for solvent.

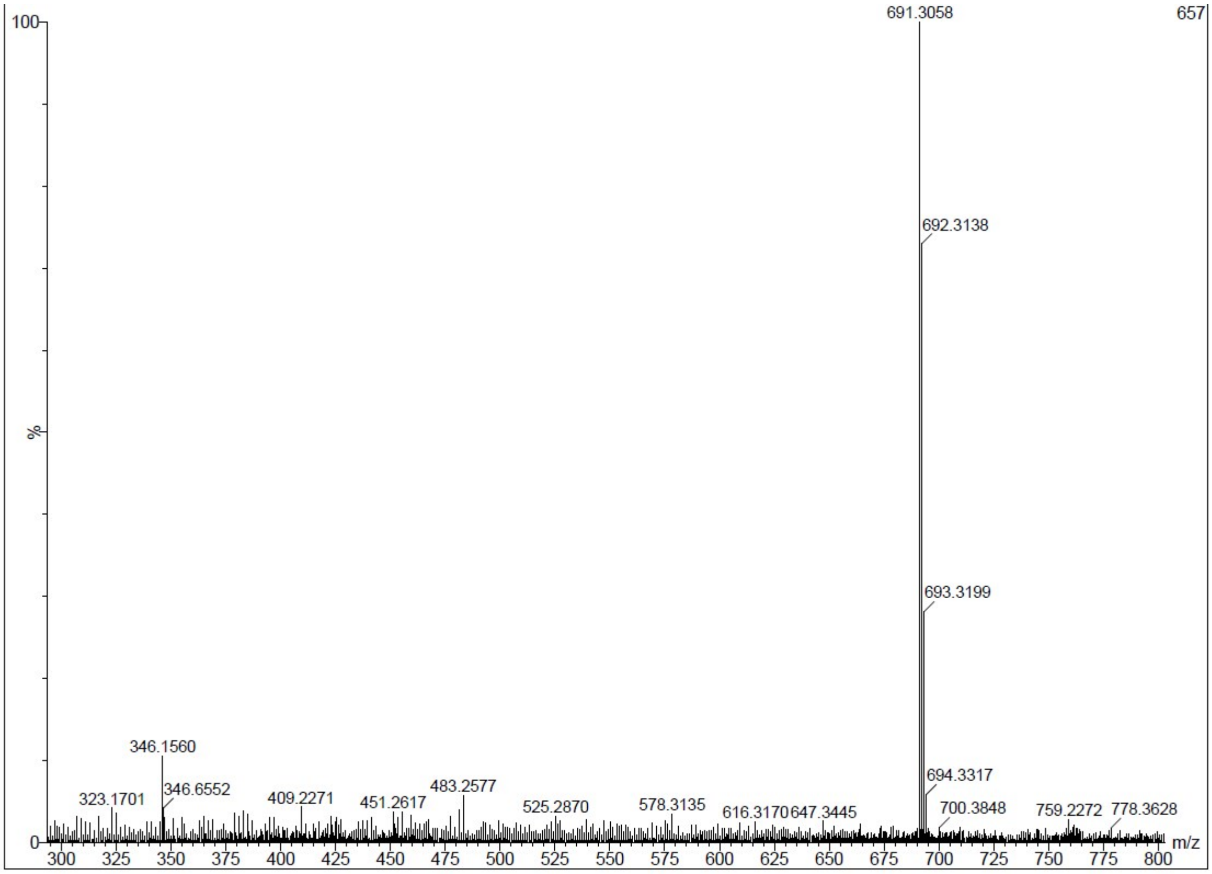


Fig. S2. ESI-HR MS of DMPH$_2$-COOH

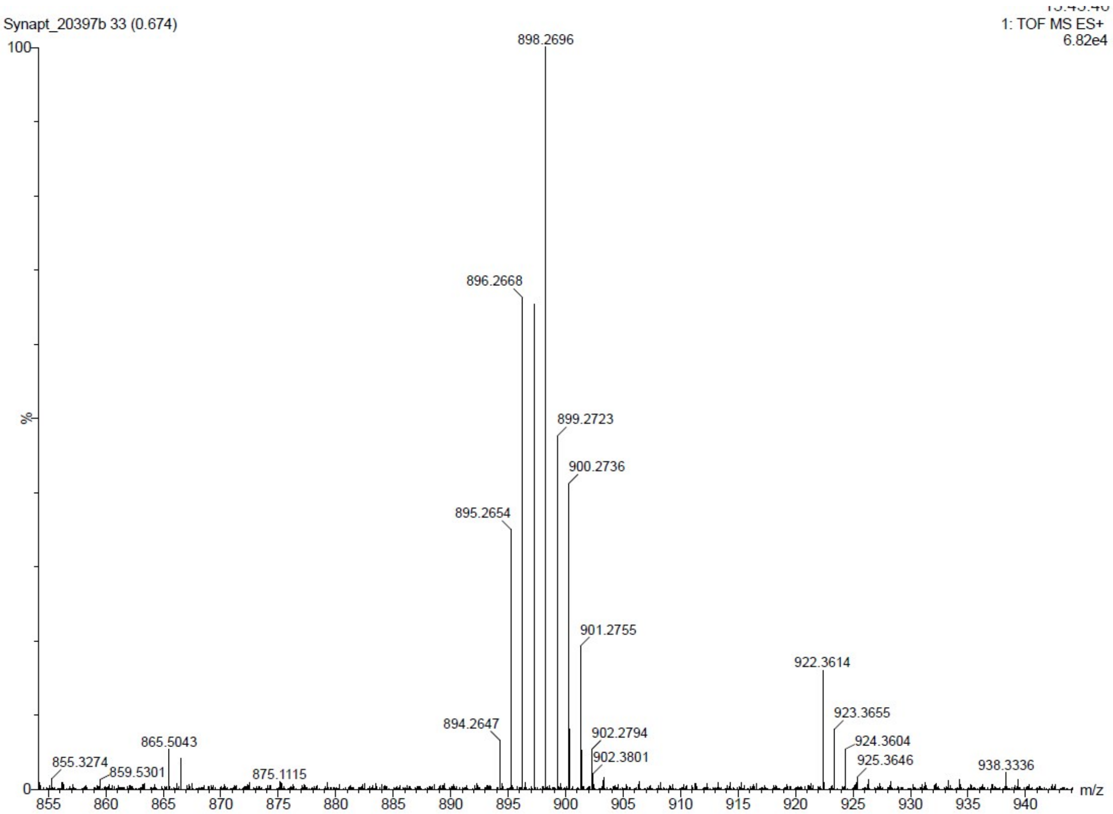


Fig. S3 ESI-HR MS of YbDMP

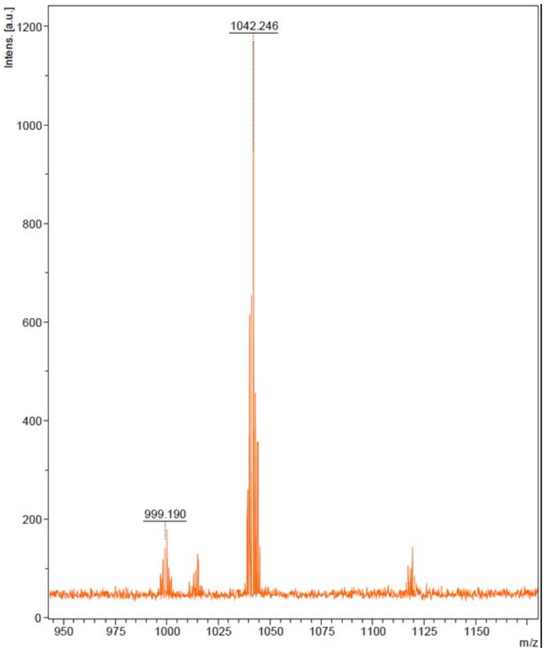
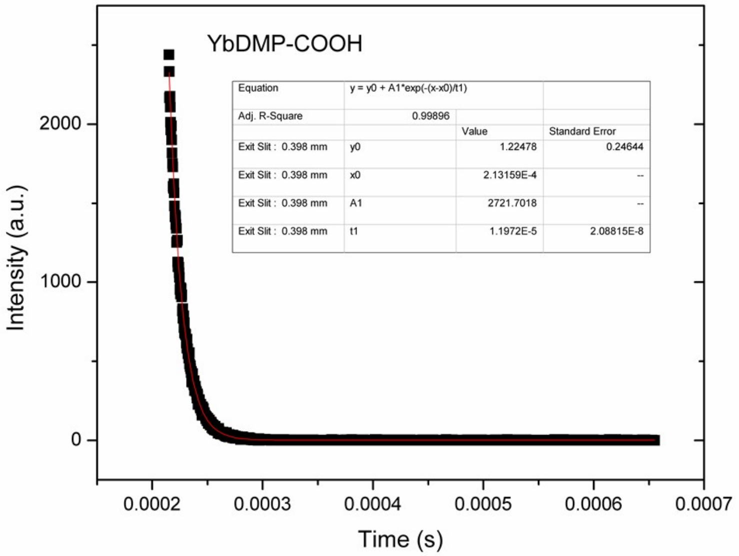


Fig. S4 MALDI MS of YbDMP-COOH

Photoluminescence Measurement. Steady state fluorescence spectra were obtained on an FS5 fluorimeter (Edinburg Instrument, Inc) with Xenon arc lamp as a light source. The decay curves of the samples in the visible region were also measured on the FS5 using single-photon-counting technology at emission maximum. A pulsed laser diode EPL 375 (Edinburg Instrument, Inc) with wavelength of 375 nm was used as light source. The lifetimes in the visible region were obtained from exponential fitting of data. The decay curves of complexes in the NIR region were recorded as we described previously.[2] Quantum yield in the visible region was measured using following equation:

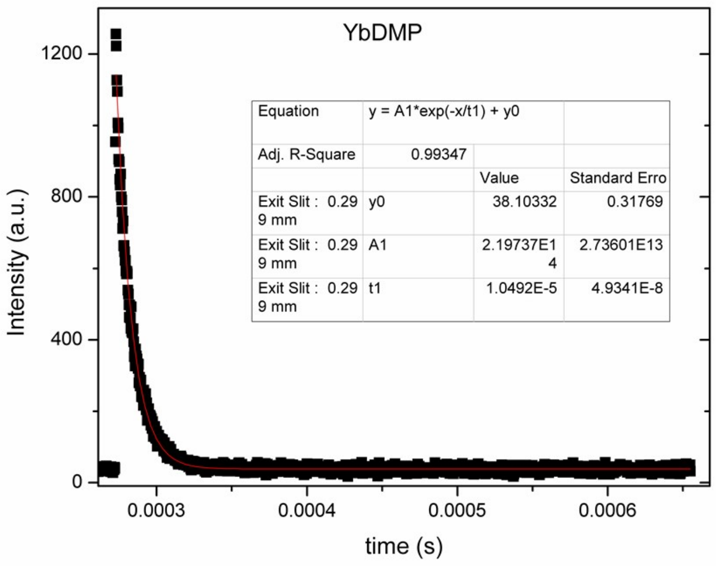
$$\Phi_X = \emptyset_{ST}\left[\frac{Grad_X}{Grad_{ST}}\right]\left[\frac{n_X}{n_{ST}}\right]^2$$

where Φ is the fluorescence quantum yield, Grad the gradient from the plot of integrated fluorescence intensity *vs* absorbance of five samples with different concentrations, and n is the refractive index of the solvents. Rhodamine 6G in ethanol ($\Phi_{ST} = 0.95$, $\lambda_{ex} = 480$ nm) was used as a reference. Quantum yields in the NIR region were determined in the same way except YbTPPTp^H was used as a reference ((Φ_{ST} = 0.032, λ_{ex} = 540 nm).[3] YbTPPTp^H was prepared as we described previously. [4]



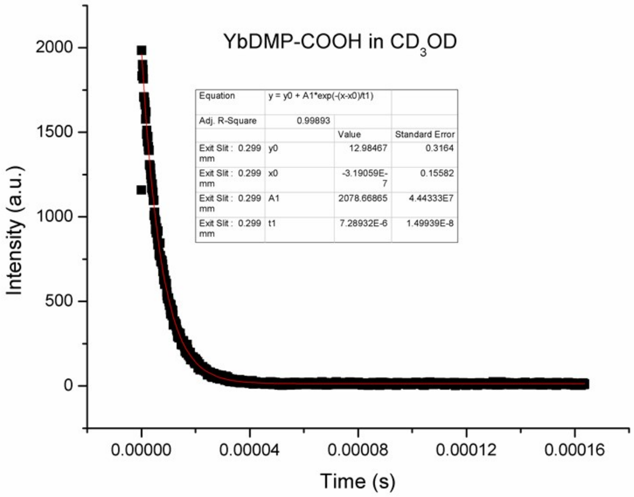
Equation	y = y0 + A1*exp(-(x-x0)/t1)		
Adj. R-Square	0.99896		
		Value	Standard Error
Exit Slit : 0.398 mm	y0	1.22478	0.24644
Exit Slit : 0.398 mm	x0	2.13159E-4	--
Exit Slit : 0.398 mm	A1	2721.7018	--
Exit Slit : 0.398 mm	t1	1.1972E-5	2.08815E-8

Figure S5 Emission decay profile of YbDMP-COOH in dichloromethane. λ_{ex} = 530 nm and λ_{em} = 980 nm



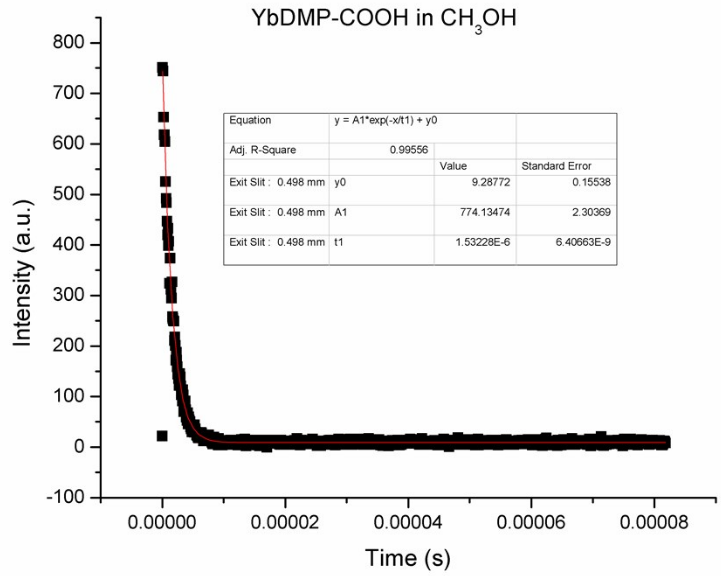
Equation	y = A1*exp(-x/t1) + y0		
Adj. R-Square	0.99347		
		Value	Standard Erro
Exit Slit : 0.299 mm	y0	38.10332	0.31769
Exit Slit : 0.299 mm	A1	2.19737E14	2.73601E13
Exit Slit : 0.299 mm	t1	1.0492E-5	4.9341E-8

Figure S6 Emission decay profile of YbDMP in dichloromethane. λ_{ex} = 541 nm and λ_{em} = 980 nm



Equation	y = y0 + A1*exp(-(x-x0)/t1)		
Adj. R-Square	0.99893		
		Value	Standard Error
Exit Slit : 0.299 mm	y0	12.98467	0.3164
Exit Slit : 0.299 mm	x0	-3.19059E-7	0.15582
Exit Slit : 0.299 mm	A1	2078.66865	4.44333E7
Exit Slit : 0.299 mm	t1	7.28932E-6	1.49939E-8

Figure S7 Emission decay profile of YbDMP-COOH in CD$_3$OD. λ_{ex} = 568 nm and λ_{em} = 980 nm



Equation	y = A1*exp(-x/t1) + y0		
Adj. R-Square	0.99556		
		Value	Standard Error
Exit Slit : 0.498 mm	y0	9.28772	0.15538
Exit Slit : 0.498 mm	A1	774.13474	2.30369
Exit Slit : 0.498 mm	t1	1.53228E-6	6.40663E-9

Figure S8 Emission decay profile of YbDMP-COOH in CH_3OH. λ_{ex} = 568 nm and λ_{em} = 980 nm

Single-crystal X-ray Diffraction Analysis. The crystals were mounted on glass fiber for data collection. Diffraction measurements were made on a CCD-based commercial X-ray diffractometer using Mo Kα radiation (λ = 0.71073 Å). The frames were collected at ambient temperature with a scan width 0.3° in ω and integrated with the Bruker SAINT software package using the narrow-frame integration algorithm. The unit cell was determined and refined by least squares upon the refinement of *XYZ*-centeroids of reflections above $20\theta(I)$. The data were corrected for absorption using SADABS program. The structures were refined on F^2 using the SHELX97. Crystal data for YbDMP·0.65 CH_2Cl_2·1.82 CH_3OH: $C_{54.47}$ $H_{50.76}$ $Cl_{1.30}$ N_6 $O_{3.82}$ Yb , MW = 1069.66, monoclinic, space group = $P_{21/c}$, a = 11.3239(9), b = 16.5128(14), c = 25.834(2) Å, β = 93.6710(10)°, V = 4820.7(7) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.474 Mgm^{-3}, μ = 2.064 mm^{-1}, F(000) = 2169, T = 100 (2) K. 47802 reflections were measured, of which 8942 were unique (R_{int} =

0.0477). Final R_1 = 0.0608 and wR_2 = 0.1187 were obtained for 7583 observed reflections with $I>2\sigma(I)$, 609 parameters, and GOF = 1.156. CCDC#: 1944838

Theoretical Calculations. Theoretical calculations were performed at a density functional theory (DFT) level using Gaussian 09 software. The initial input structures were built using structure builder tools. The ground state geometries of ligands were optimized using 6-31G(d) as basis set for non-metal elements and MWB28 for Yb, and B3LYP as functional in CH_2Cl_2 using CPCM to mimic the solvent effect All other parameters were default set. No negative frequency was found in the final optimized structures. The time-dependent (TD) DFT calculations were carried out using the same basis sets and functional in dichloromethane.

Table S1. Molecular orbital surface profiles of HOMO and LUMO

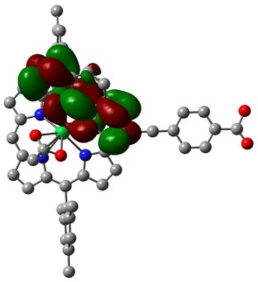
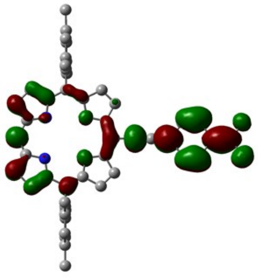
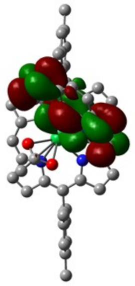
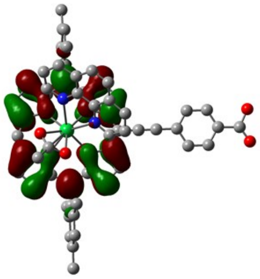
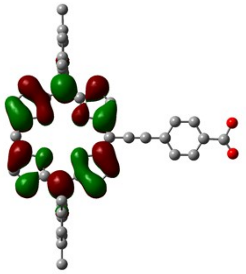
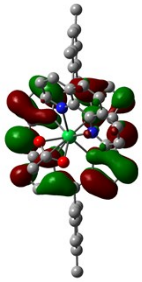
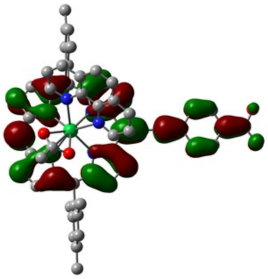
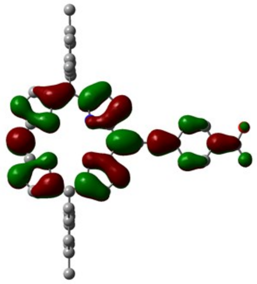
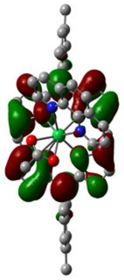
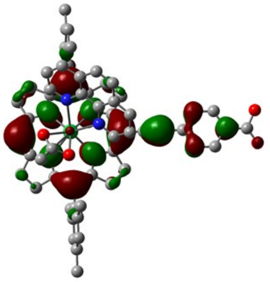
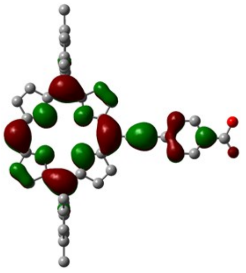
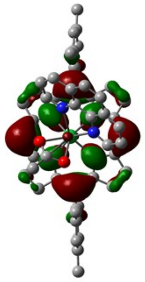
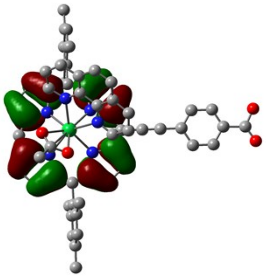
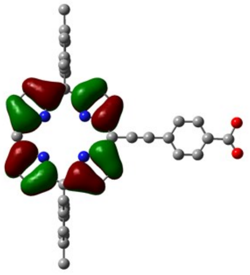
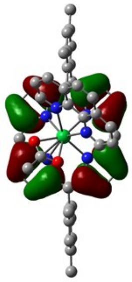
	YbDMP-COOH	DMPH$_2$-COOH	YbDMP
LUMO+2			
LUMO+1			
LUMO			
HOMO			
HOMO-1			

Table S2. Selected transitions (with Oscillation >0.02) of DMPH2-COOH from calculation

Wavelength (nm)	Oscillation Strength	Symmetry	Transitions(contribution)
659	0.9938	Singlet State	HOMO->LUMO (94%) H-1->L+1 (4%)
598	0.0612	Singlet state	H-1->LUMO (39%), HOMO->L+1 (58%)
461	1.496	Singlet state	H-1->LUMO (57%), HOMO->L+1 (38%)
434	1.4407	Singlet state	H-1->L+1 (69%), HOMO->L+2 (14%) H-6->LUMO (7%), H-4->LUMO (2%), H-1->LUMO (2%), HOMO->LUMO (3%)
407	0.0318	Singlet state	H-6->LUMO (22%), H-4->LUMO (39%), HOMO->L+2 (37%)
392	0.1562	Singlet state	H-7->LUMO (62%), HOMO->L+2 (12%) H-8->LUMO (5%), H-6->LUMO (8%), H-1->L+1 (6%)
387	0.0331	Singlet state	H-8->LUMO (29%), H-7->LUMO (31%), H-6->LUMO (13%), HOMO->L+2 (16%) H-4->LUMO (3%), H-1->L+1 (5%)

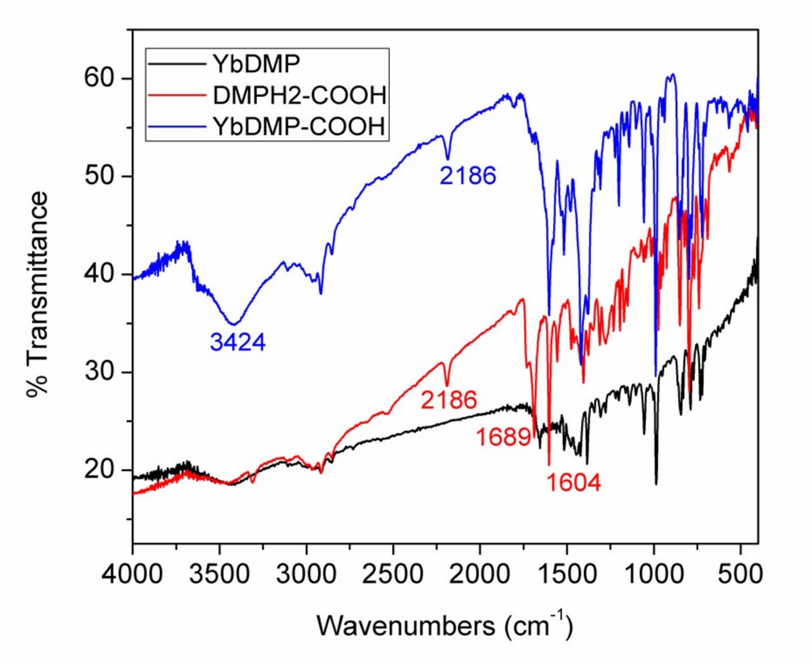


Fig. S9. FT-IT spectra of YbDMP, DMPH$_2$-COOH and YbDMP-COOH (KBr pellets were used for measurements).

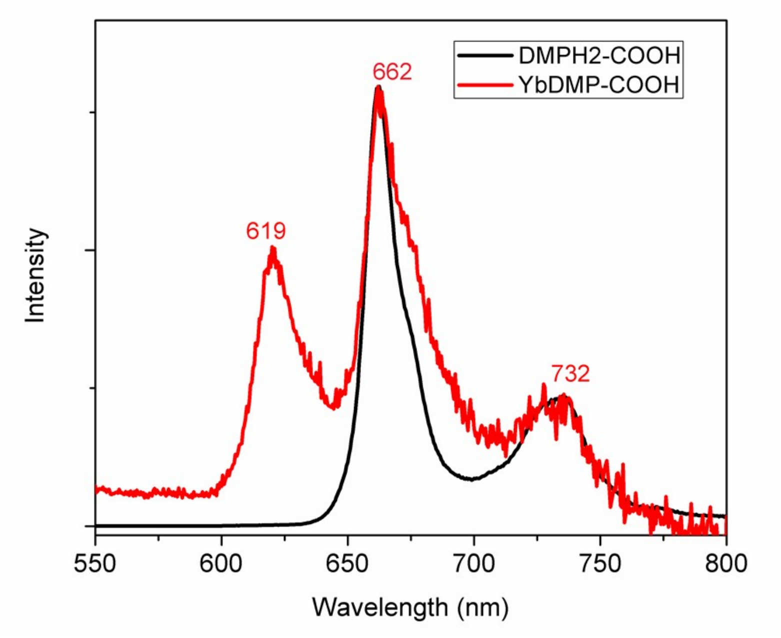


Fig. S10. Normalized emission of DMPH$_2$-COOH and YbDMP-COOH in DCM at room temperature.

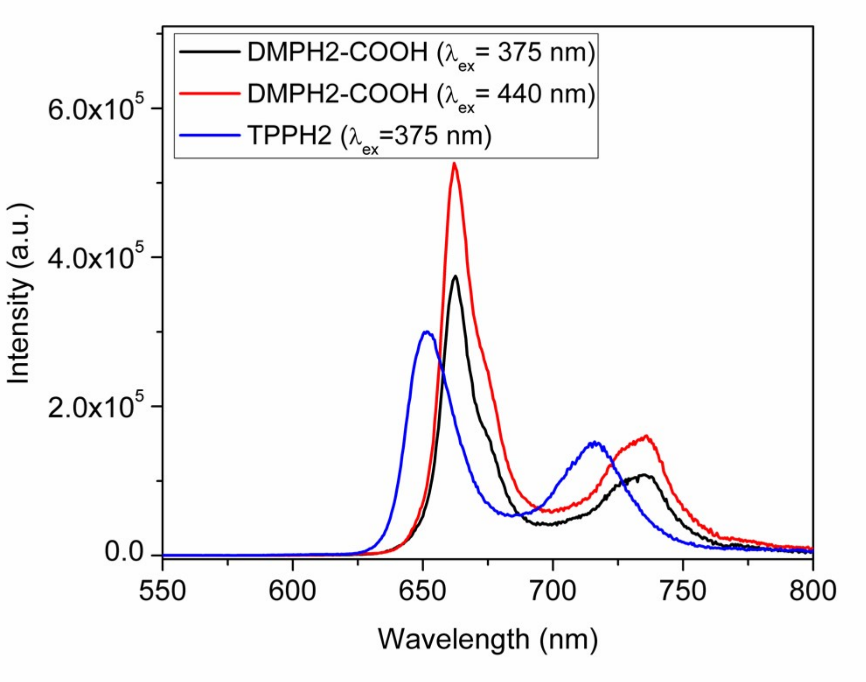


Fig. S11. Emission spectra of DMPH$_2$-COOH and TPPH$_2$ in DCM upon excitation at different wavelengths.

References

1. L. Si, H. He and K. Zhu, *New J. Chem.*, 2014, **38**, 1565-1572.
2. H. He, P. S. May and D. Galipeau, *Dalton Trans.*, 2009, 4766-4771.
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