Supplementary Information for

Unusual Near White Electroluminescence of Saddle Shaped Porphyrin Emitting Diods

Hashem Shahroosvand*[a] , Saeed Zakavi [b], , Ahmad Sousaraei [a], Ezeddin Mohajerani [c] Malek Mahmoudi [c]

[a] Chemistry Department, University of Zanjan, Zanjan, Iran.

[b] Department of Chemistry , Institute for Advanced Studies in Basic Sciences, Gavazang, Zanjan, Iran.

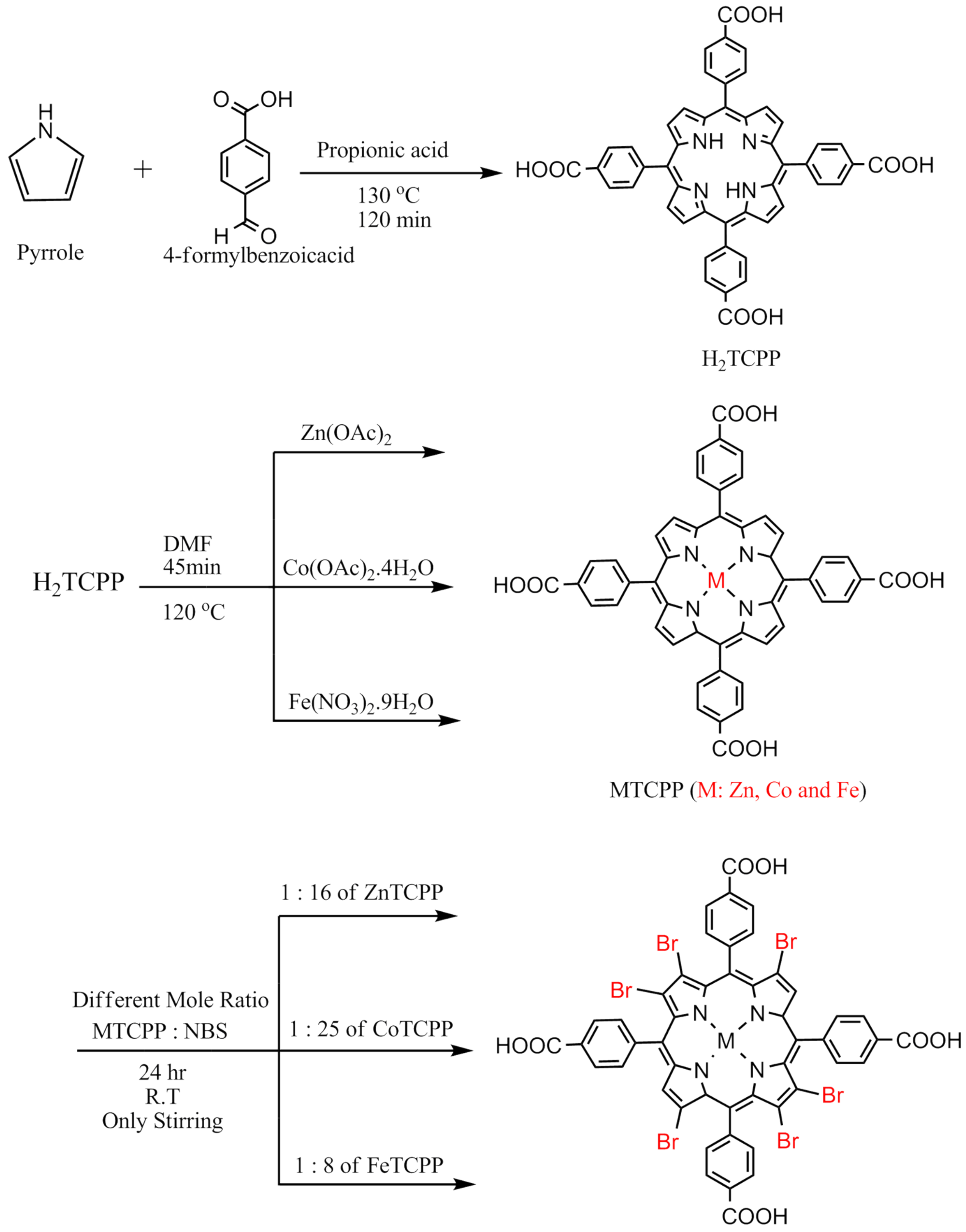
[c]Laser and Plasma Research Institute, Shahid Beheshti University, Tehran, Iran.

Content:

S1a: Synthesis of porphyrins and metalloporphyrins

Meso-tetrakis(4-phenylcarboxyl)porphyrin (H_2TCPP) was prepared according to the literature methods [1a]. The signal of H_β of H_2TCPP appears at δ 8.87 in DMSO-d_6. Also, the resonance due to the ortho and meta protons of the meso aryl substituents is observed at δ 8.34-8.41 ppm. The N-H and –COOH protons are observed at δ -2.93 and 13.24 (a very broad signal), respectively. The metal complexes, MTCPP (M = Fe(II), Zn(II) and Co(II)), were prepared by standard methods by the reaction of the H_2TCPP and metal salts in DMF [1b]. H_2TCPP (100 mg, 126 mmol) and metal (II) acetate (150 mmol) were dissolved in DMF (20 mL), and the solution was stirred at reflux for 45 min. The metal complex formation was monitored spectrometrically in DMF. If the reaction is not complete, another gram of the metal salt was added. After filtration, the residue was washed with water to remove excess metal salt. The bromination of MTCPP was perfomed according to the literature [1c] with some modifications. The reaction of MTCPP and freshly recrystallised N-bromosuccinimide (NBS) [1c] in 1:16 molar ratio in THF for a reaction time of 24 h gave the corresponding β brominated metalloporphyrin (see ESI, S3). Finally, THF was evaporated and the residue was washed with water then purified with chloroform and water by separatory funnel (ESI†, S1b-d) and was characterized by UV-vis (Fig. 1) and/ or ^1H NMR spectroscopy and ICP analysis. With the exception of the closed shell metals such as zinc(II) and nickel(II) and some Cu(II) porphyrins, the metal complexes of meso-tetraarylporphyrins are usually high spin and consequently paramagnetic. Therefore, the NMR spectroscopy cannot be used to characterize the metal complexes of porphyrins. The signal of the β protons of $ZnTCPP_6$ was observed at δ 8.05 ppm. Also, the ortho and meta protons appear at δ 7.53-7.82 ppm in DMSO-d_6. The degree of bromination of ZnTCPP and H_2TCPP have been determined by ^1H NMR spectrometry based on the ratio of the intensities of the signals corresponding to the protons from H_β and meso substituents (H_β/H_{ortho} and H_β/H_{meta} ratios); in the case of $ZnTCPPBr_{6\ and}$ H_2TCPP, a value of ca. 0.25 was observed for both the H_β/H_{ortho} and H_β/H_{meta} ratios. In the case of the Co(II) and Fe(II) complexes, degree of bromination of the porphyrin ligand was determined after the dematallation with CF_3COOH [1c] of metal complexes and extraction of the brominated free base porphyrin, i.e. $H_2TCPPBr_6$. In the case of $H_2TCPPBr_6$, the β protons appear at δ 8.60 in DMSO-d_6. The substitution of six β positions with electronegative bromine atoms was expected to shift the resonance due to the remaining two β protons downfield. The observed upfield shift of H_β clearly shows the out of plane deformation of the porphyrin core [2] of $H_2TCPPBr_6$. Similar upfield shift of the β protons was previously reported for β-hexa-brominated porphyrins [3]. The broader signal observed for the β protons of $H_2TCPPBr_6$ in comparsion with that of H_2TCPP suggests the formation of two steroisomers of $H_2TCPPBr_6$. In other words, the remaining β protons may be on the adjacent or opposite pyrrole rings. It should be noted that the β protons of H_2TCPP and other symmetically substituted porphyrins appears as a nearly sharp signal at room temperature [4]. Also, the resonance due to the ortho and meta protons of the meso aryl substituents was observed at δ 8.37-8.45 ppm and the N-H protons were observed at δ -1.30 ppm. On the other hand, Furthermore, ICP analysis was used to confirm the elemental composition of the brominated metalloporphyrins.

S1b: Scheme of synthesis of complexes



S1c. Material and instruments

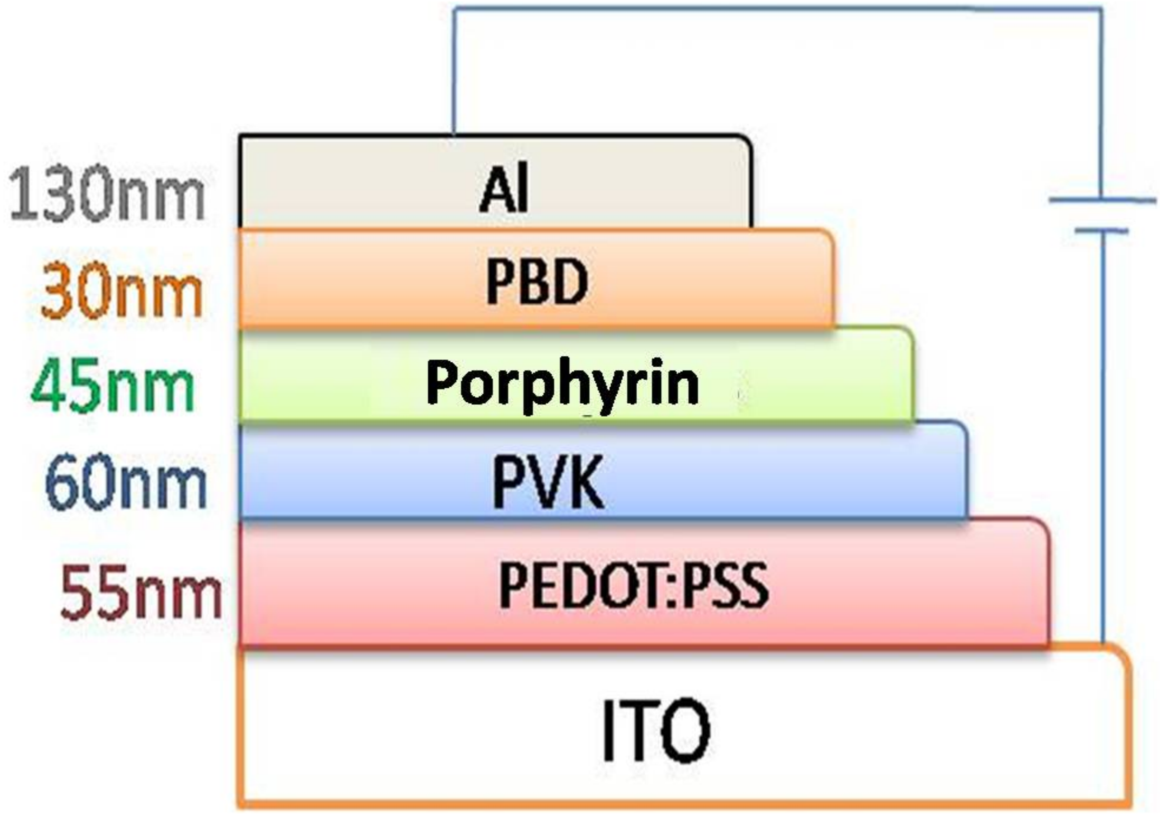
All chemicals and solvents were purchased from Merck & Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 597 spectrometer ^{1}H-NMR spectra were recorded by use of a Bruker 400 MHz, spectrometer..

The molecular and electronic structure calculations were performed with density functional theory (DFT) using the Gaussian 03(G03) program package. The B3LYP functional [5] with the LANL2DZ basis set was carried out. All geometry optimizations were performed in either C1 or C2 symmetry with subsequent frequency analysis to show that the structures are at the local minima on the potential energy surface. The electronic orbitals were visualized using GaussView 3.0.

S1d. Preparation of EL devices and testing

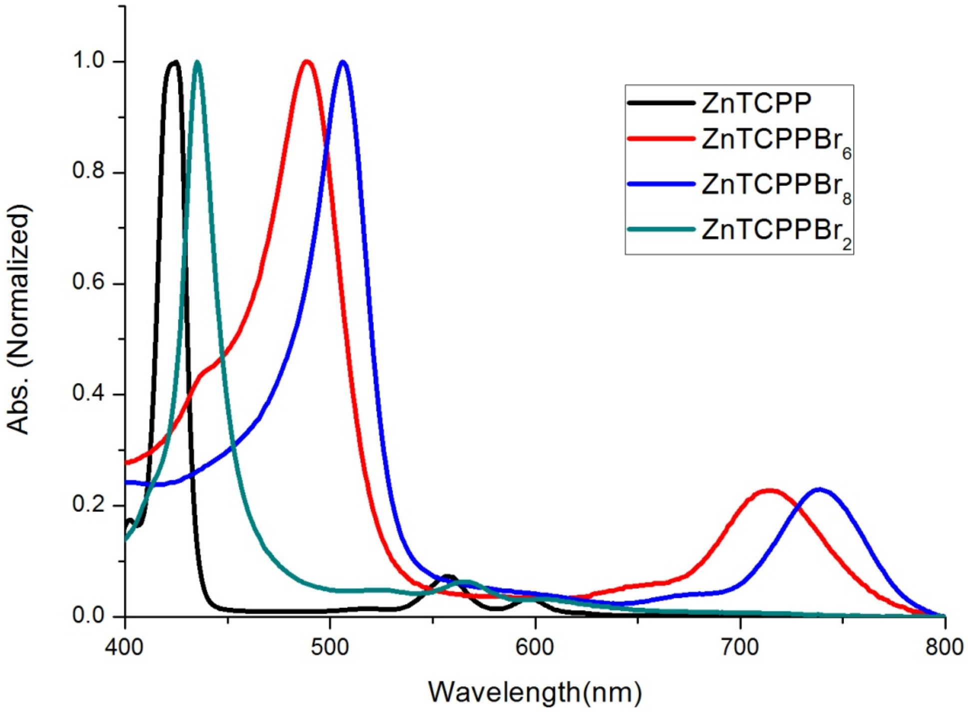
The structure of the fabricated device is as follow:

ITO/PEDOT:PSS(55nm)/PVK (60nm) /PBD(30nm)/Al(130nm)and, ITO/PEDOT:PSS(55nm)/ porphyrin complex (45nm)/Al(130nm), That is shown in below figure .

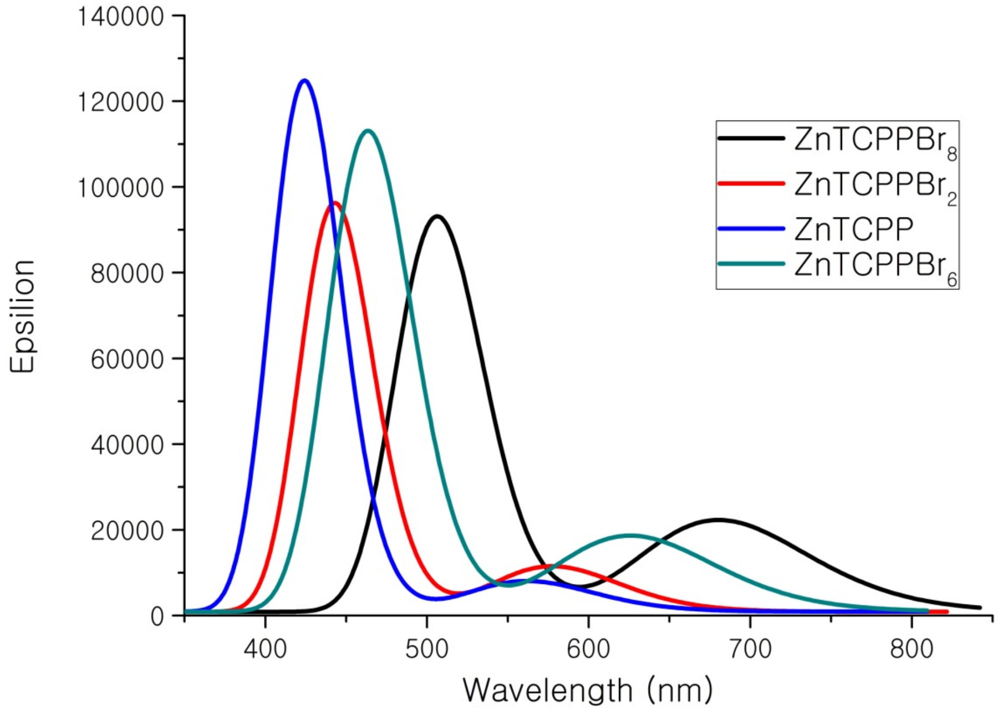


PVK as a hole-transporting and PBD as an electron-transporting material were uesd. Glass substrates, coated with ITO (sheet resistance of 70 Ω/m^2), were used as the conducting anode PEDOT: PSS(poly(3,4-ethylenedi-oxythiophene):poly(styrenesulfonate)) was used as a hole injection and transporting layer. All polymeric layers were successively deposited onto the ITO coated-glass by using spin-coating process from the solution. A metallic cathode of Al was deposited on the emissive layer at 8×10^{-5} mbar by thermal evaporation. The PEDOT: PSS was dissolved in DMF, spin coated on ITO and was held in an oven at 120 ^{o}C for 2 hours after deposition. PVK, PBD and porphyrin complexes with weight ratio of 0.03: 0.004: 0.01 were separately dissolved in 8 mL of DMF, and then spin coated and baked at 80°C for 1 hour. The thickness of the polymeric thin film was determined by a Dektak 8000. The EL intensity and spectra were measured with an ocean optic USB2000, under ambient conditions. In addition, Keithley 2400 source meter was used to measure the electrical characteristics of the devices.

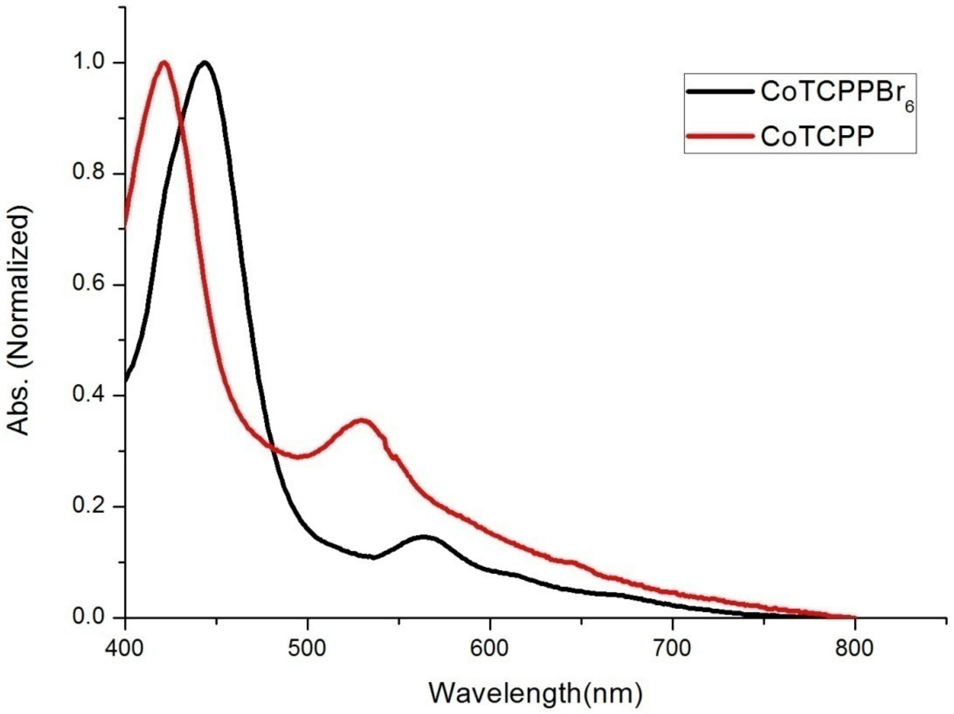
S2a. Absorption spectra of ZnTCPP, $ZnTCPPBr_2$, $ZnTCPPBr_6$ and $ZnTCPPBr_8$ in THF solution 10^{-5} mol lit^{-1}.



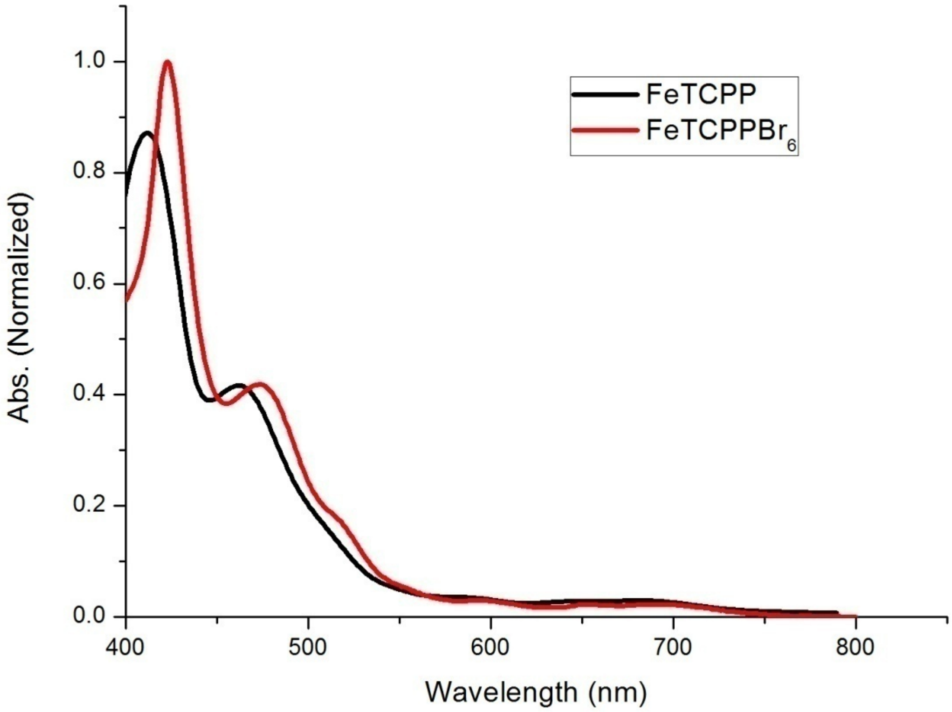
S2b. Absorption spectra of ZnTCPP, $ZnTCPPBr_2$, $ZnTCPPBr_6$ and $ZnTCPPBr_8$ obtained at the TD-DFT/(LanL2DZ) level of theory.



2c. Absorption spectra of CoTCPP and $CoTCPPBr_6$ in THF solution 10^{-5} mol lit^{-1}.



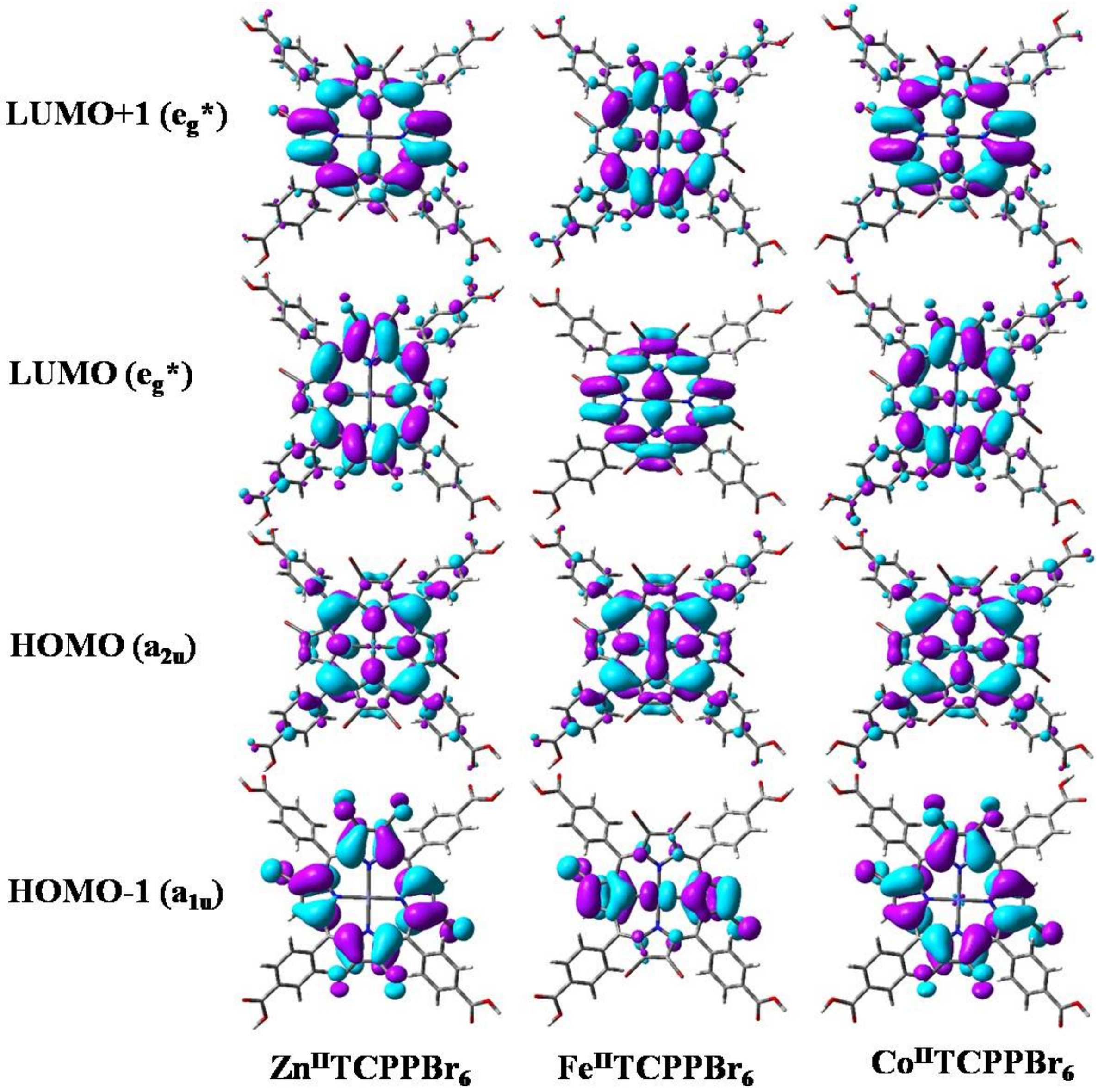
S2d. Absorption spectra of FeTCPP and $FeTCPPBr_6$ in THF solution 10^{-5} mol lit^{-1}.



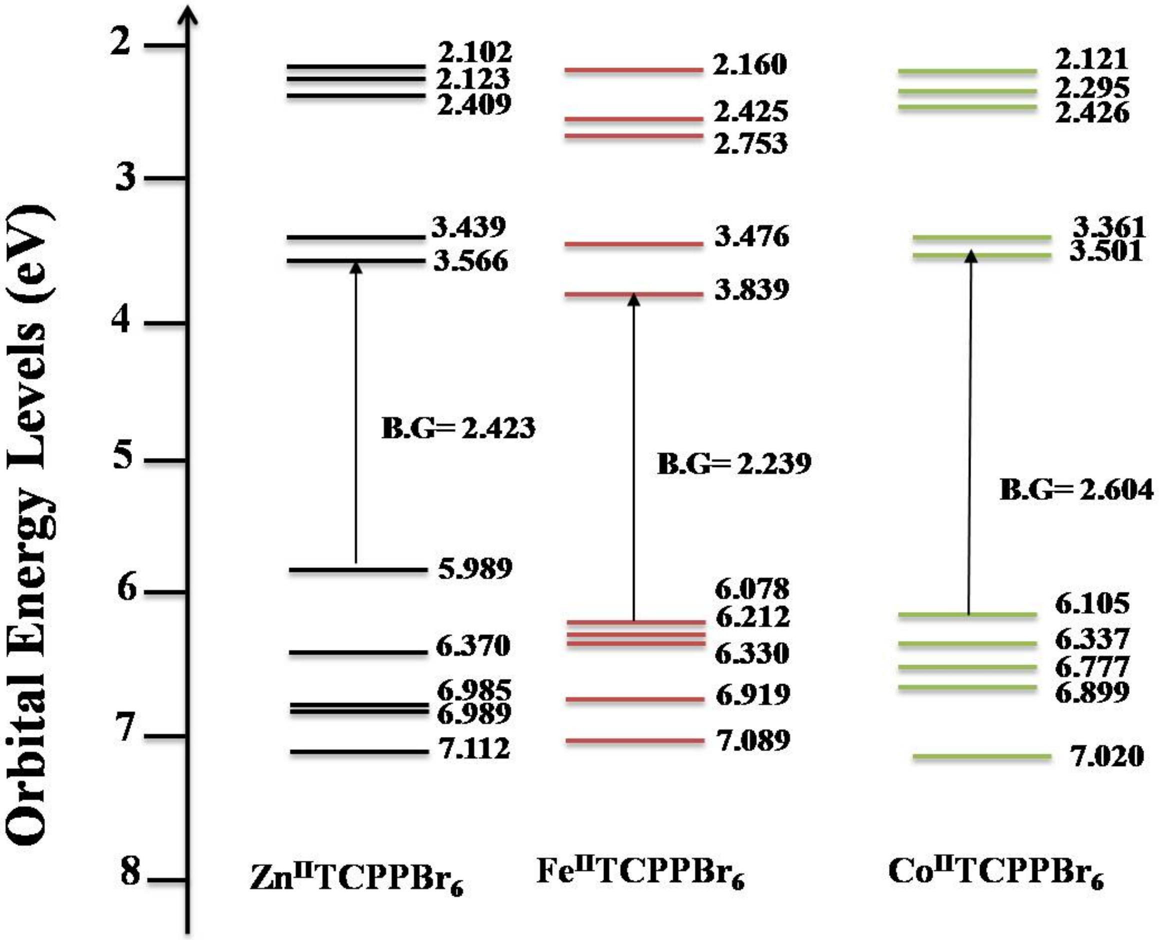
S3: UV-vis results of various bromination experiments to obtain optimized reaction.

No.	ZnTCPP:NBS Molar Ratio	Soret band (B) (nm)	Q band (nm)	Red Shift (nm)	Compounds
1	1:0	423	556, 598	…………	ZnTCPP
2	1 : 4	435	566, 606	(B: 12 nm), (Q: 10, 8 nm)	$ZnTCPPBr_2$
3	1 : 8	435	566, 606	(B: 12 nm), (Q: 10, 8 nm)	$ZnTCPPBr_2$
4	1 : 12	435	566, 606	(B: 12 nm), (Q: 10, 8 nm)	$ZnTCPPBr_2$
5	1 : 16	489	715	B: 66 nm	$ZnTCPPBr_6$
6	1 : 20	489	715	B: 66 nm	$ZnTCPPBr_6$
7	1 : 25	492	718	B: 69 nm	$ZnTCPPBr_8$
8	1 : 30	492	718	B: 69 nm	$ZnTCPPBr_8$
9	1 : 40	492	718	B: 69 nm	$ZnTCPPBr_8$
10	1 : 50	492	718	B: 69 nm	$ZnTCPPBr_8$
11	1 : 60	492	718	B: 69 nm	$ZnTCPPBr_8$
Opt.	**1:16 opt**	**489**	**715**	**B: 66 nm**	$\mathbf{ZnTCPPBr_6}$

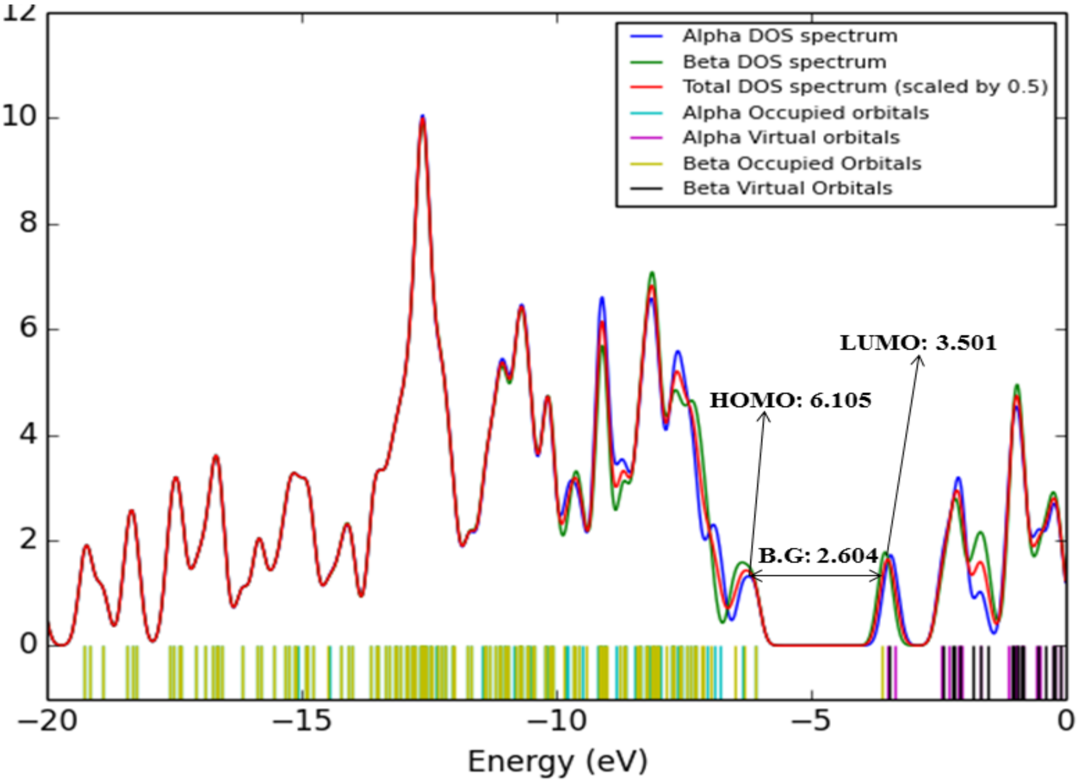
S4. Isodensity plots for selected occupied and unoccupied molecular orbitals (HOMO, LUMO, HOMO+1 and LUMO+1) of MTCPPBr$_6$ (M= Fe, Co and Zn) by DFT calculations.



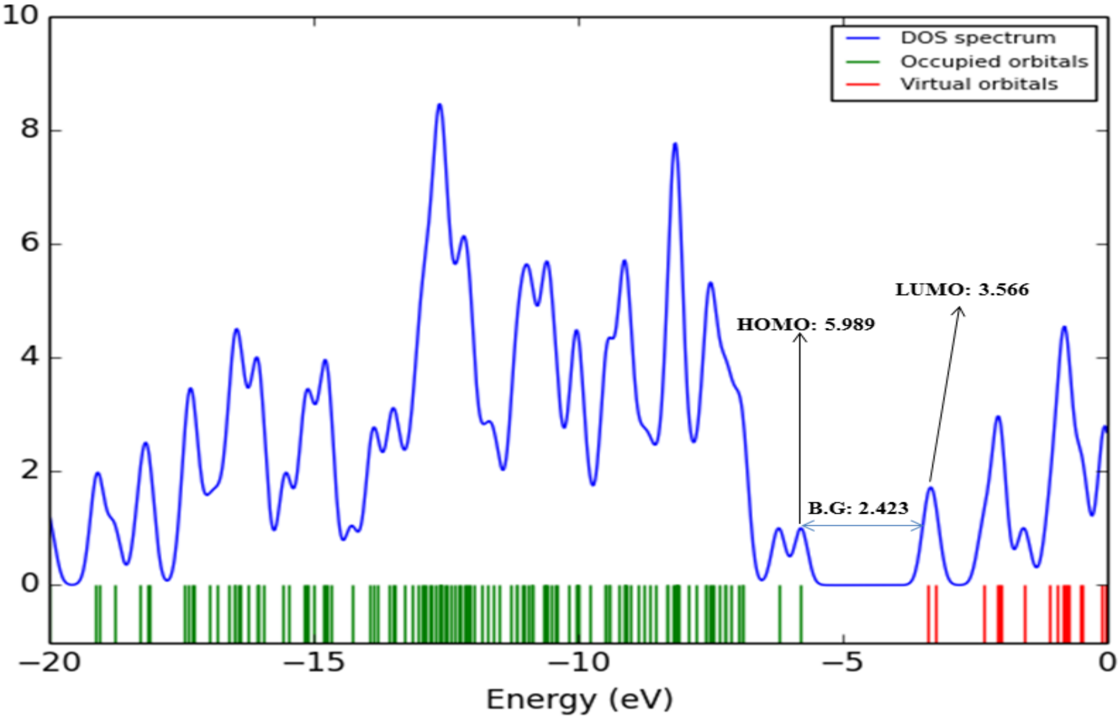
S5. Diagram of the five highest occupied and five lowest unoccupied molecular orbital levels of $MTCPPBr_6$ (M=Fe, Co, Zn)



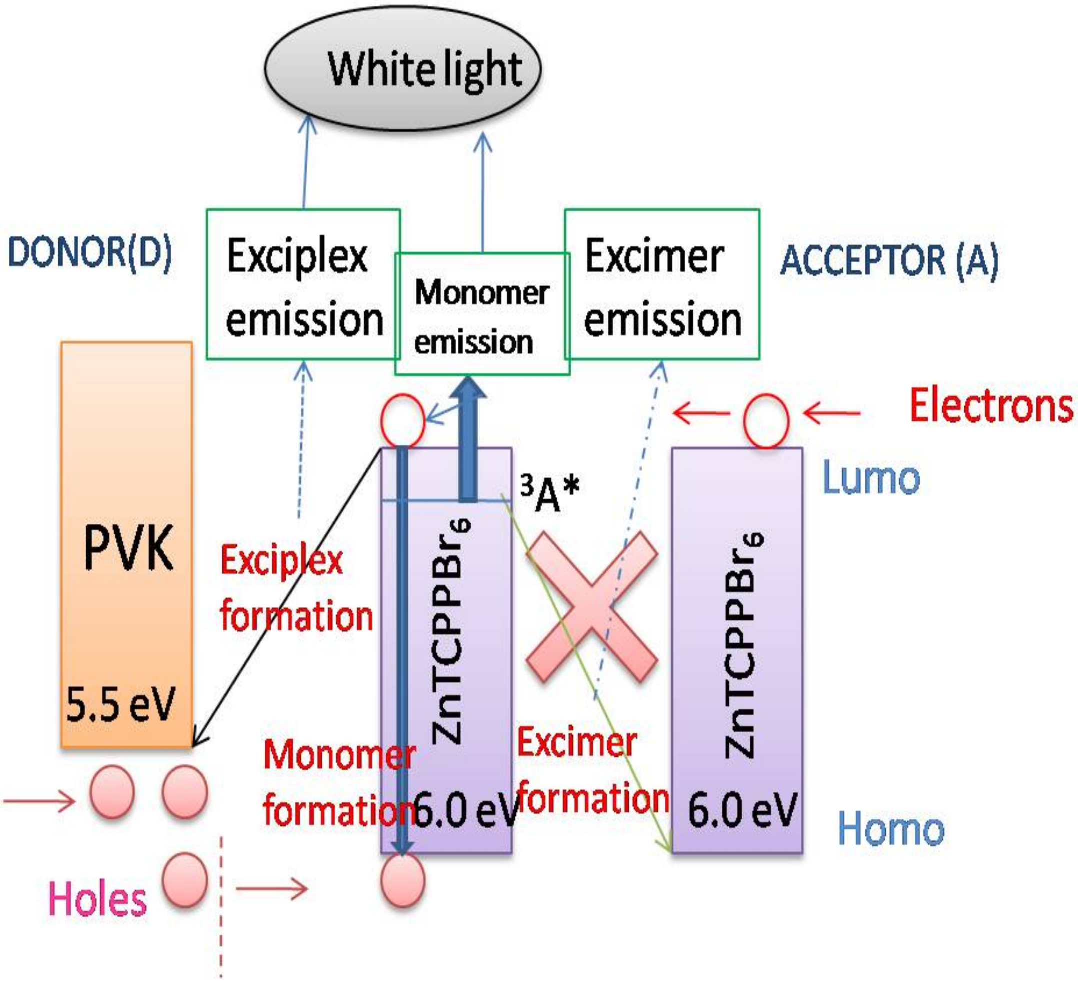
S6. DOS diagram of $Co^{II}TCPPBr_6$.



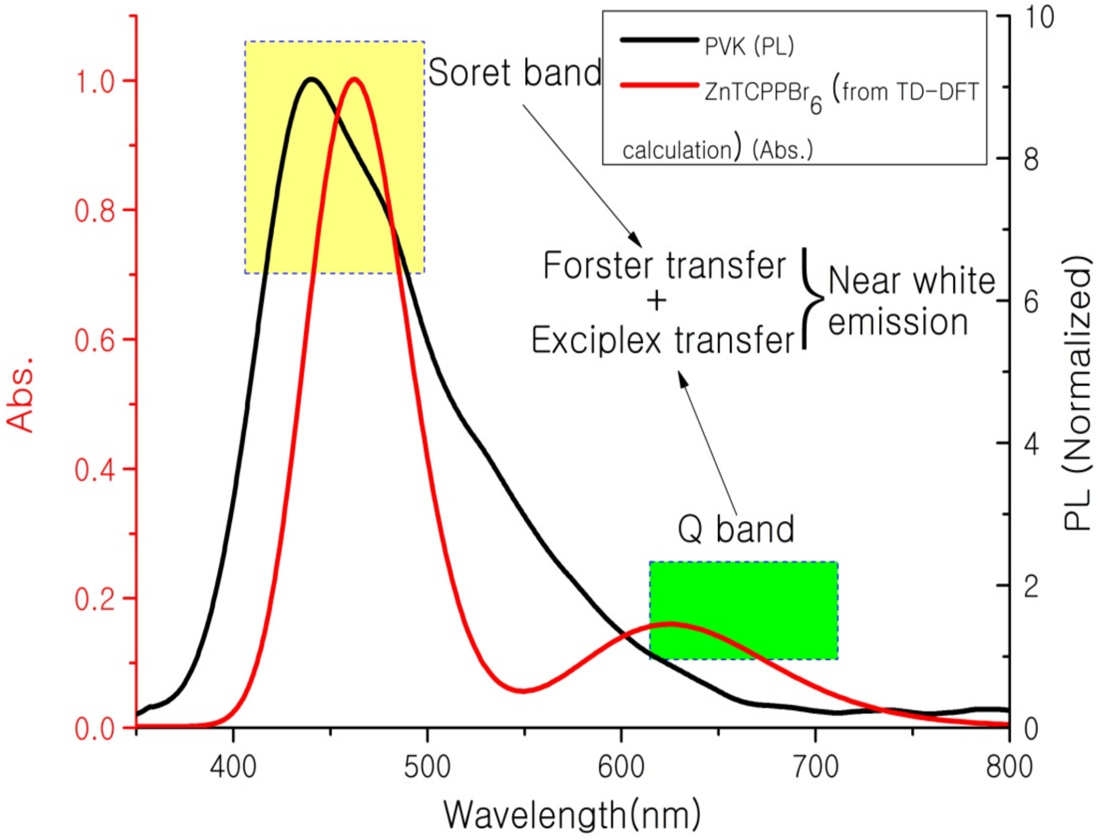
S7. DOS diagram of $ZnTCPPBr_6$.



S8. The possibility of the Exciplex, Excimer and Forster transfers in porphyrin devices.



S9. The contribution of Soret and Q bands to produce Forster and Exciplex transfers



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