Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

New Supramolecular Compounds Based on Porphyrin and Polyoxometalate: Synthesis, Characterization and Nonlinear Optical and Optical Limiting Properties

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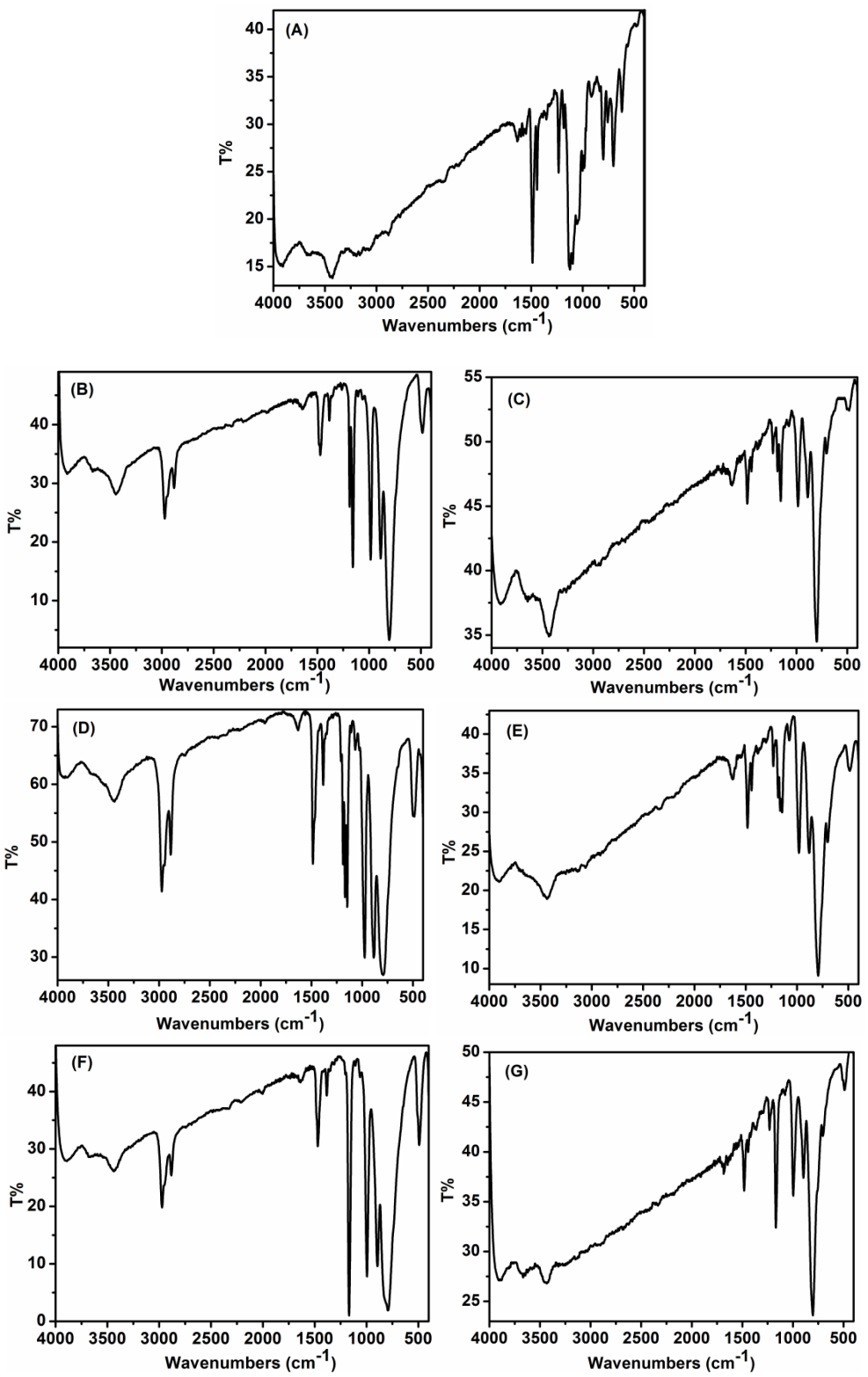

Fig. S1. IR spectra of $[H_2TPP][ClO_4]_2$ (A), SWV_1 (B), compound **1** (C), SWV_2 (D), compound **2** (E), SW (F) and compound **3** (G).

Table S1. IR data of $[H_2TPP][ClO_4]_2$, parent POMs (SWV_1, SWV_2 and SW) and compounds **1** - **3**

$[H_2TPP][ClO_4]_2$	Compound **1**	Compound **2**	Compound **3**	Assignment
3308	3305	3302	3304	ν(N-H)
3070	3069	3063	3066	$\nu(C_\beta\text{-H})^{p}_{sym}$
3106	3094	3095	3098	$\nu(C_\beta\text{-H})^{p}_{asym}$
1490	1483	1482	1480	$\nu(C_a\text{-}C_m)_{sym}$
1441	1439	1439	1438	Phenyl
1228	1233	1231	1233	$\delta(C_\beta H)_{asym}$
	1185/1153	1144/1162/1183	1154	S-O_a
	(1088/1157)	(1147/1169/1186)	(1167)	
	985	974	984	W-O_t
	(986)	(980)	(996)	
	886	879	884	W-O_b-W
	(887)	(886)	(896)	
	798	784	800	W-O_c-W
	(806)	(792)	(816)	

Annotation: symbols ν and δ denote stretching, in-plane bending modes, respectively. The subscripts sym and asym represent the symmetric and asymmetric modes, respectively. Superscript *p* denotes protonated pyrrole. The data in the parentheses are IR data of the corresponding parent POMs.

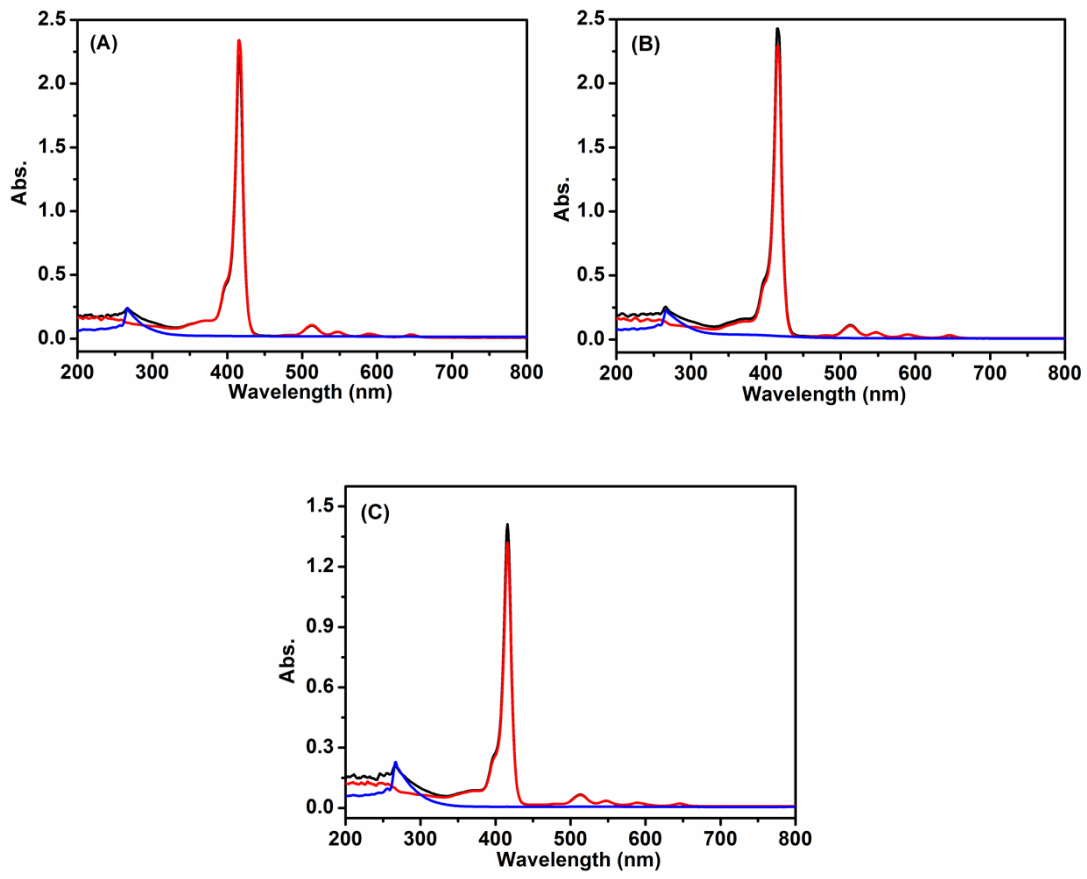

Fig. S2. UV-spectra of (A) compound **1**, SWV_1, $[H_2TPP][ClO_4]_2$; (B) compound **2**, SWV_2, $[H_2TPP][ClO_4]_2$; (C) compound **3**, SW, $[H_2TPP][ClO_4]_2$ in DMF. Color code: black, the compounds **1**, **2**, or **3**, respectively; red, $[H_2TPP][ClO_4]_2$; blue, parent POMs. The concentrations of compounds **1** – **3** and parent POMs are 4.4×10^{-6} mol·L^{-1}, and concentration of $[H_2TPP][ClO_4]_2$ is 6.6×10^{-6}, 8.8×10^{-6} and 4.4×10^{-6} mol·L^{-1} for spectra (A), (B) and (C), respectively.

Table S2. Molar extinction coefficient value of the compounds **1-3** and $[H_2TPP][ClO_4]_2$ at 266 and 416 nm.

	1 (266nm)	**1** (416 nm)	**2** (266 nm)	**2** (416 nm)	**3** (266 nm)	**3** (416 nm)	$[H_2TPP][ClO_4]_2$ (416 nm)
$\varepsilon/(10^5)$ ($L \cdot mol^{-1} \cdot cm^{-1}$)	0.54 (0.53)	3.34	0.56 (0.52)	2.84	0.50 (0.51)	3.18	3.06

Annotation: the data in the parentheses are the value of the corresponding parent POMs.

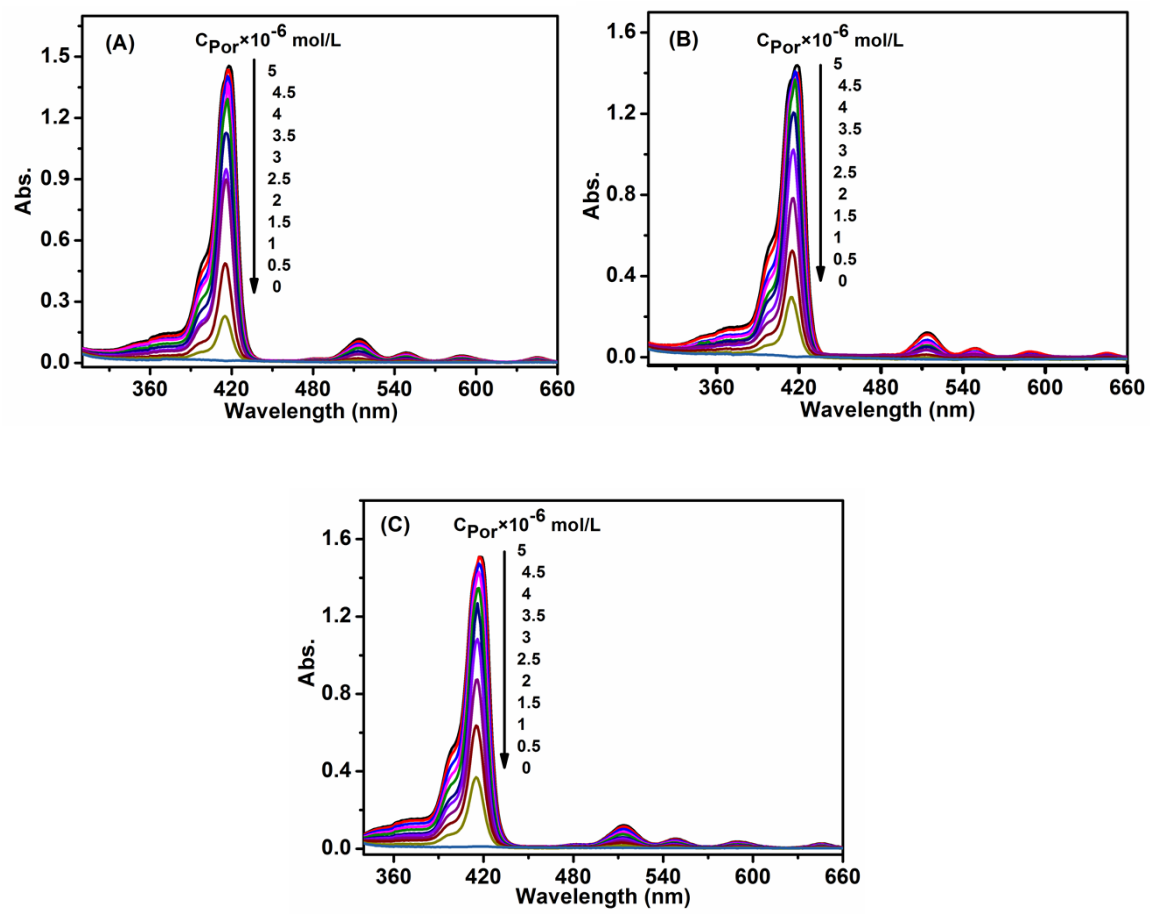

Fig. S3. The UV-vis spectra of the ($[H_2TPP][ClO_4]_2$ + SWV_n) solutions (in $CHCl_3/CH_3CN$, V:V = 1:1) with varying molar ratios of $[H_2TPP][ClO_4]_2$ and SWV_1 (A), SWV_2 (B), and SW (C). Note: [Porphyrin] + [POM] = 5×10^{-6} mol·L^{-1} for all cases.

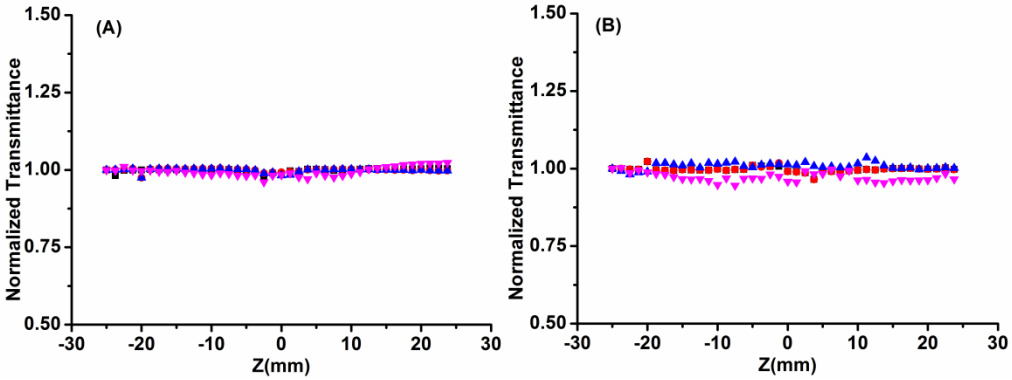

Fig. S4. The Z-scan curves of pristine DMF and parent POMs solution in DMF. (A) open-aperture curves; (B) closed-aperture curves. Color code: red, SWV_1; black, SWV_2; blue, SW; pink, DMF.

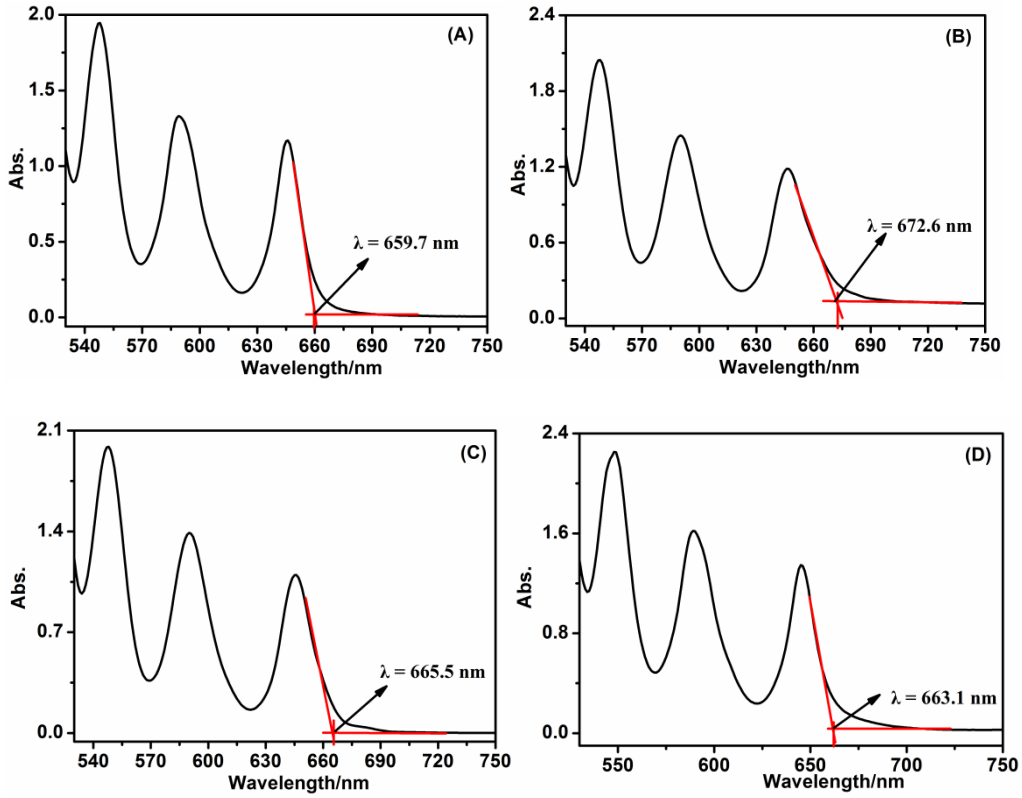

Fig. S5. UV-vis spectra of $[H_2TPP][ClO_4]_2$ (3.0 mmol·L^{-1}) (A), **1** (B), **2** (C) and **3** (D) (2.5 mmol·L^{-1}) in DMF highlighting the absorption edges corresponding to the HOMO-LUMO gap E_g values of $[H_2TPP][ClO_4]_2$ and compounds **1** – **3**, respectively.

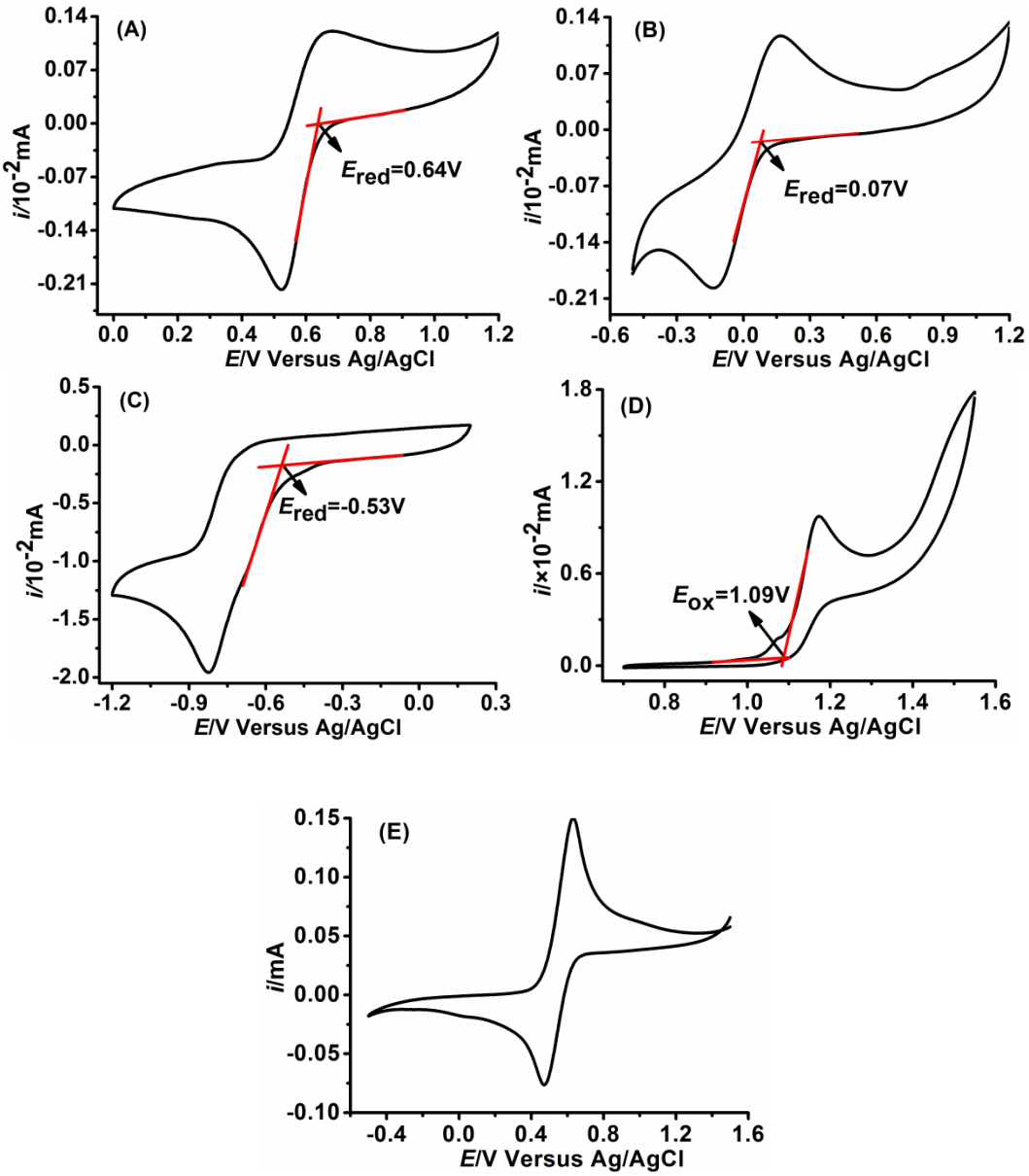

Fig. S6. CV spectra of parent SWV_1 (A), SWV_2 (B), SW (C), $[H_2TPP][ClO_4]_2$ (D) and ferrocene (E) in dry DMF (all the compounds have the concentrations of 1 mmol·L^{-1}).