**Covalent Synthesis of Two Hybrids Composed of Dawson-type Polyoxometalate and Porphyrin with Remarkable Third-order Optical Nonlinearities Reflecting the Effect of Polyoxometalates**

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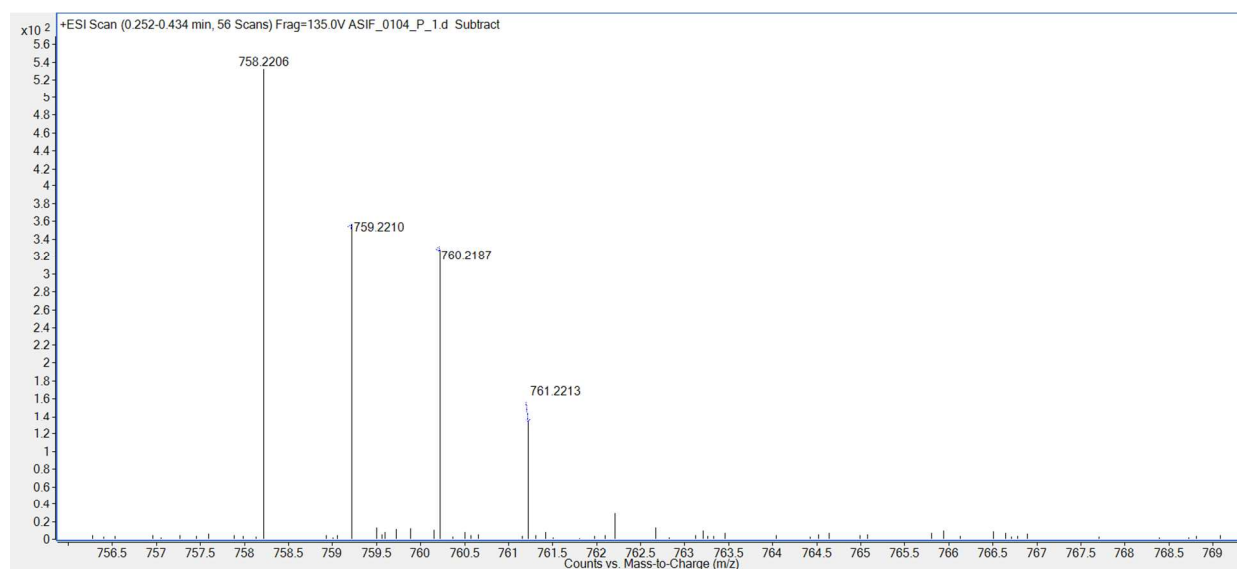
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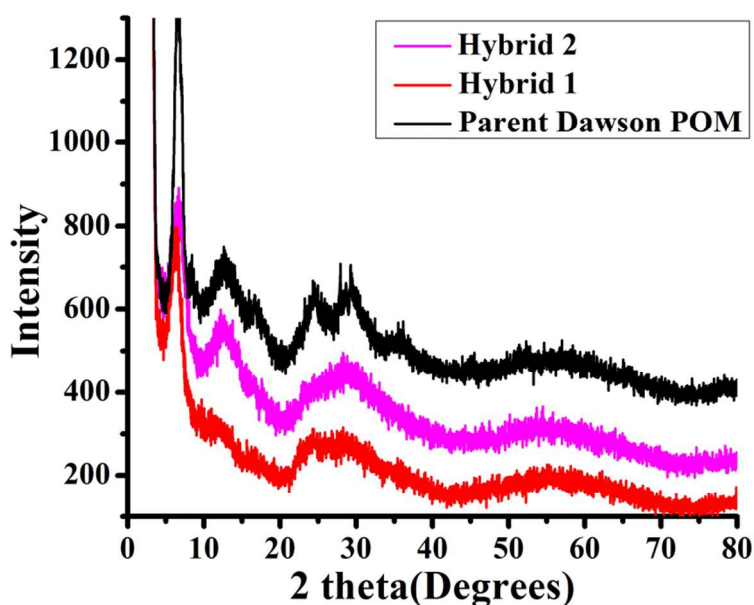
Figure S1. Powder XRD pattern of hybrids **1** and **2** with parent Dawson POM.
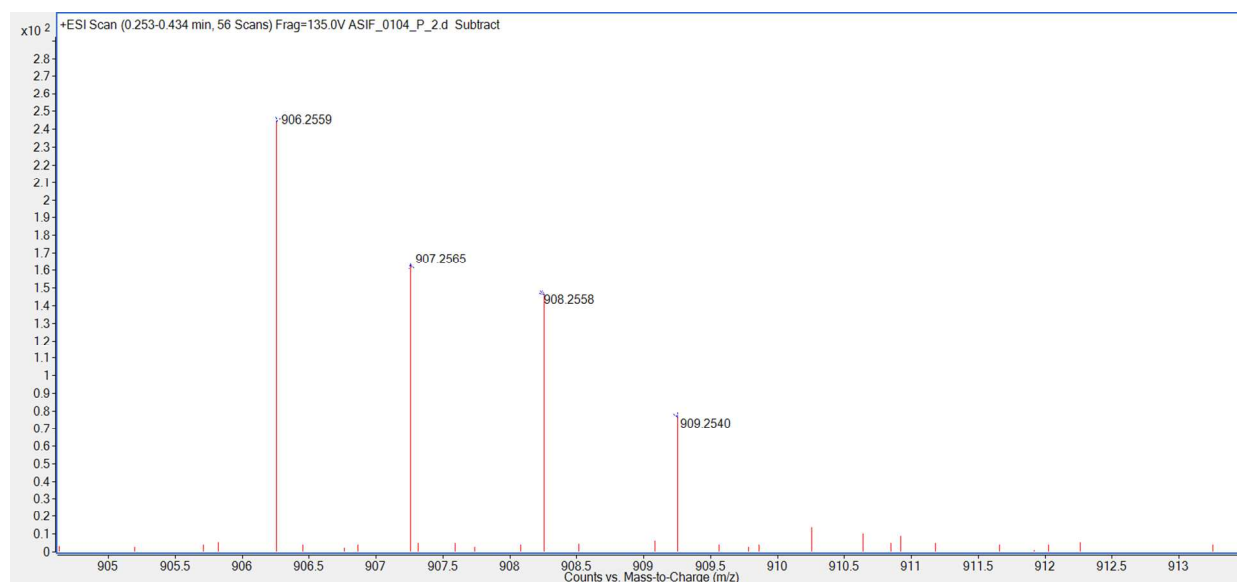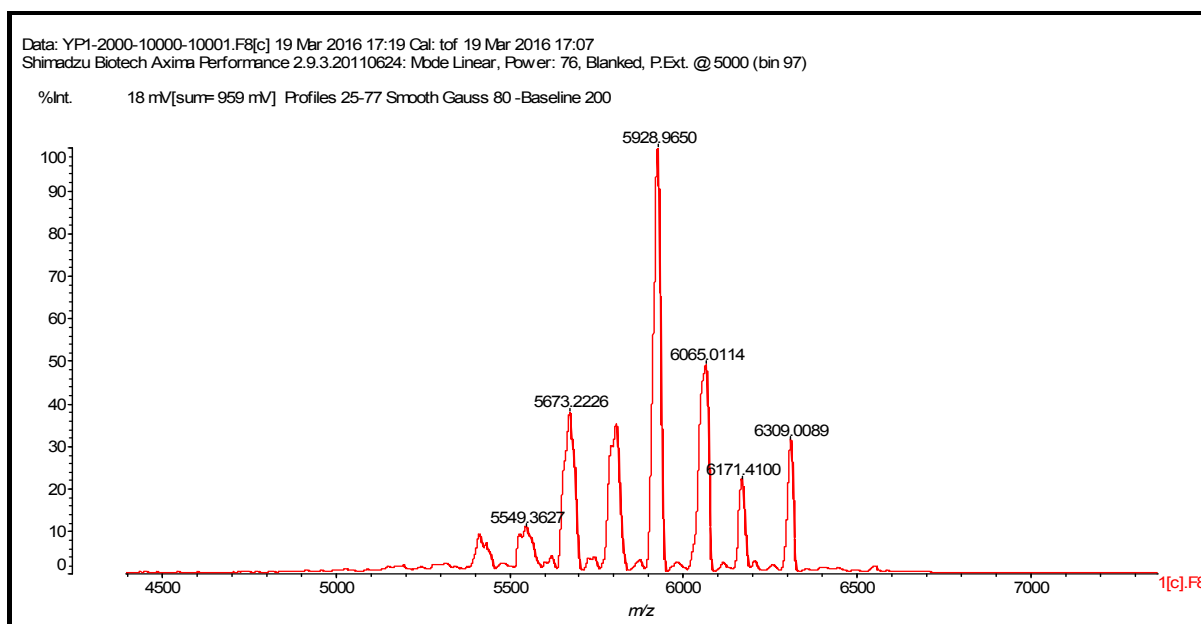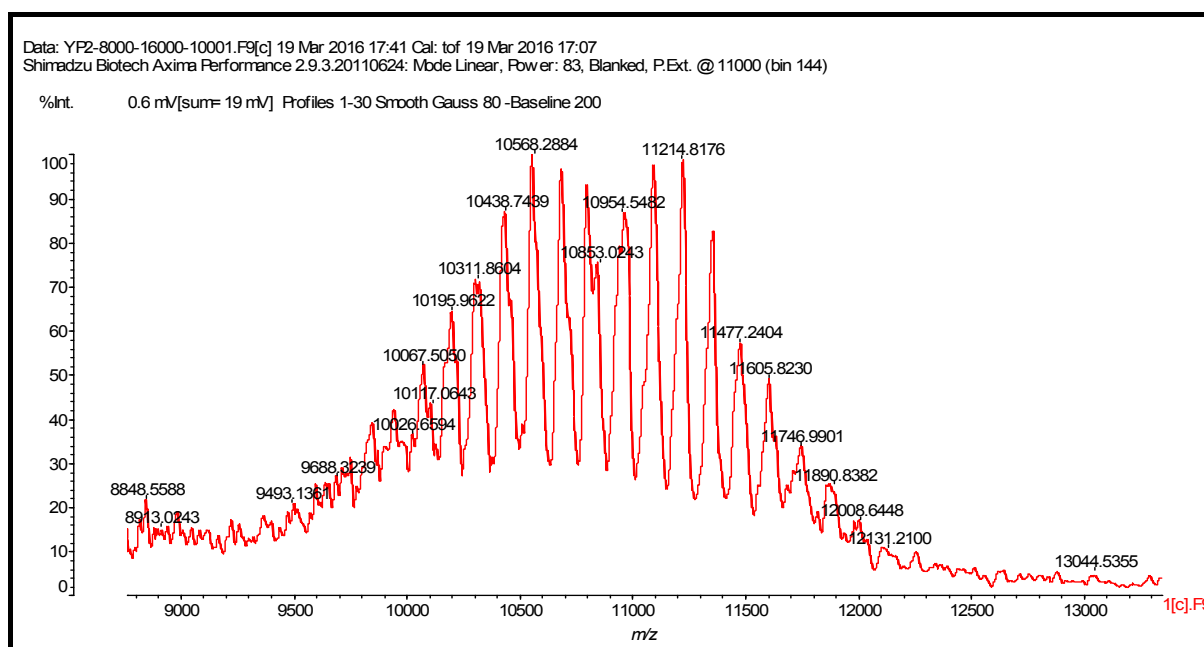
(a)

(b)

Figure S2. ESI-MS spectra of TPP-di-Tris (a) and TPP-Tris (b).

(a)

(b)

Figure S3. MALDI-TOF-MS spectra of hybrid **1** (a) and hybrid **2** (b).

Synthesis of TPP-Tris: TPP-Tris was prepared as previously reported[1-2] but with a minor modification. In detail, 5,10,15-(4-phenyl)-20-(4-carboxymethylphenyl)porphyrin[3] (1mmol), K_2CO_3 (0.083 g, 1 mmol) and Tris-hydroxylaminomethane (1mmol) were introduced in a 2 ml

flask. DMSO (2 mL, dried on molecular sieves) was added and the mixture was protected from light and stirred for 17h under Nitrogen at 85 ^{0}C. The mixture was poured in cold distilled water (100 mL), the resulting precipitate was collected by simple filtration, adsorbed on silica gel and purified by flash chromatography, elution with a gradient from chloroform + methanol (4:2) to yield the expected product as a violet powder (0.295 g, 50 % yield). Elemental analysis (%) calcd. for: $C_{49}H_{39}N_5O_4$.MeOH : C 67.23, H 5.08, N 7.84; found: C 67.53, H 5.15, N 4.73 N 7.76. (ESI-MS) m/z 762.6 (M+1) [+]. ^{1}H NMR (400 MHz; DMSO-d6): δ = 8.84 − 7.83 [All phenyl + pyrrole 'H'], 7.69 (s, 1H, 2NH), 4.90 (s, 3H, OH), 3.85 (s, 6H, CH_2), -2.91 (s, 2H, -NH). FT-IR (KBr): ν_{max} = 3324 (ν_{O-H}, m, br), 2946, 2894 (ν_{C-H}, w), 2324 (w), 1722 (w), 1644 ($\nu_{C=O}$, vs) 1597 (m), 1531 (s), 1498 (m), 1470 (ν_{C-H}, sh), 1400 (sh), 1348 (m), 1320 (br), 1229 (w), 1198 (m),1156 (w),1105 (m), 1052 (s), 960 (sh) 886 (m), 870 (sh), 804 (vs) , 758 (m), 737 (s), 668 (w), 567 (m) cm^{-1}. UV–vis spectrum (λ_{max} (nm) in DMF/CH$_3$CN: 415, 512, 548, 589, and 645.
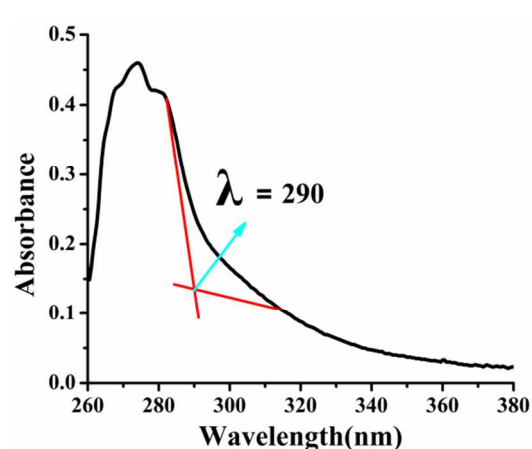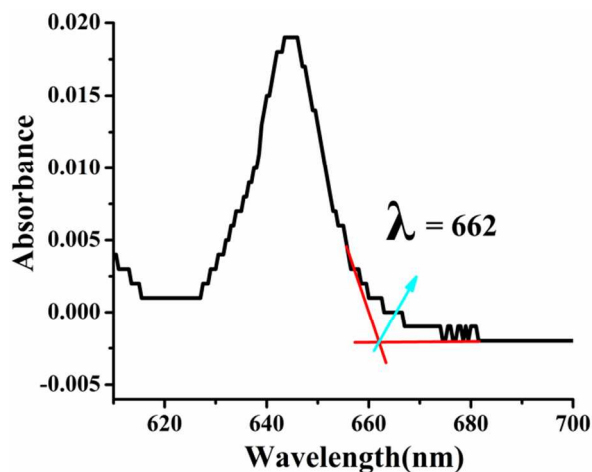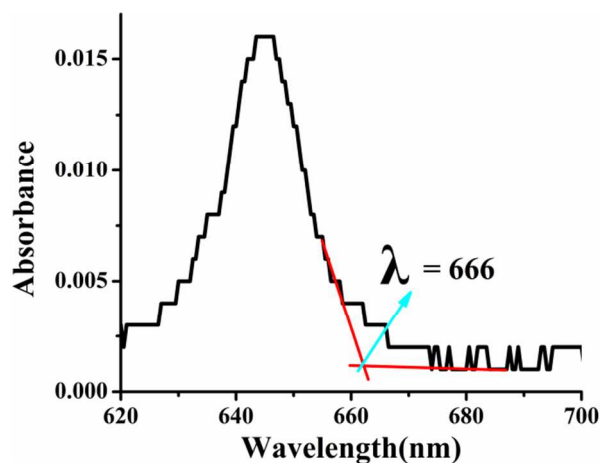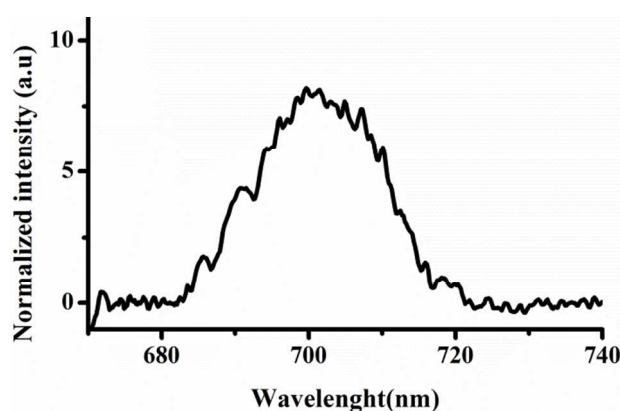

(a)
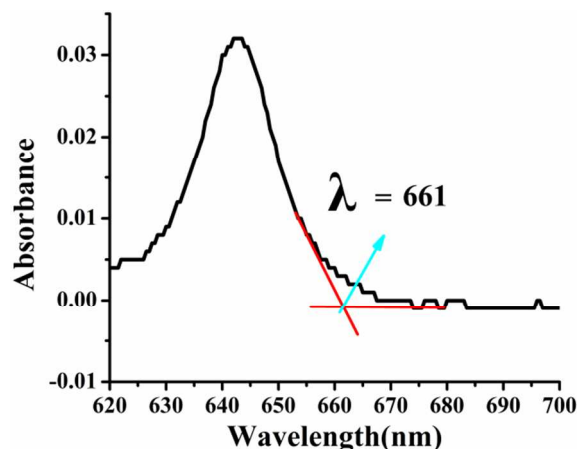
(b)
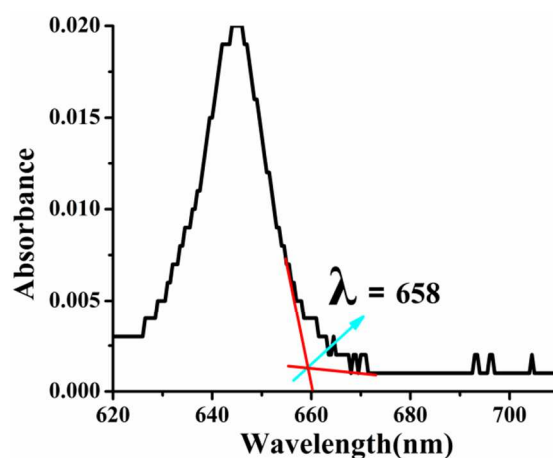
(c)

(d)

(e)

Figure S4. UV-vis. spectra of Dawson POM (a), TPP-di-Tris (b), TPP-Tris (c), Hybrid **1** (d), Hybrid **2** (e) in DMF/CH$_3$CN (all the compounds have the concentration of 5.32×10^{-5} M, highlighting the absorption edges corresponding to the HOMO-LUMO gap E_g values of the compounds, respectively.

(a)
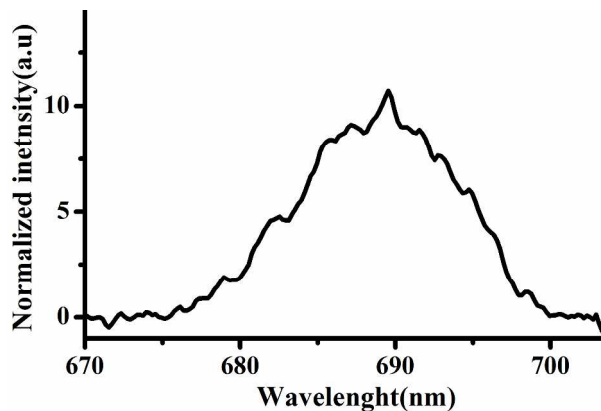
(b)

Figure S5. Phosphorescence spectra of 10^{-5} M solutions of hybrid **1** (a) and hybrid **2** (b) in DMF/CH$_3$CN (v/v = 1:1) at the excitation wavelength λ_{exc}= 331 and 328 nm respectively.

Calculation of the estimated energy level of the singlet excited state, triplet excited states, and charge-separated state

According to the formula E(singlet) = (1240/lambda(lowest Q) – 1240/lambda(fluorescence))/2 (eV), the energy levels of singlet excited states of all hybrids and porphyrin molecules are calculated:

E(singlet) for TPP-di-Tris = ((1240/661) – (1240/649))/2 (eV) = -0.020 eV

E(singlet) for TPP-Tris = ((1240/658) – (1240/648))/2 (eV) = -0.016 eV

E(singlet) for Hybrid **1** = ((1240/662) – (1240/651))/2 (eV) = -0.015 eV

E(singlet) for Hybrid **2** = ((1240/666) – (1240/649))/2 (eV) = -0.025 eV

According to the formula E(triplet) = (1240/lambda(lowest Q) – 1240/lambda(phosphorescence))/2 (eV), the energy levels of triplet excited states of hybrids **1** and **2** are calculated:

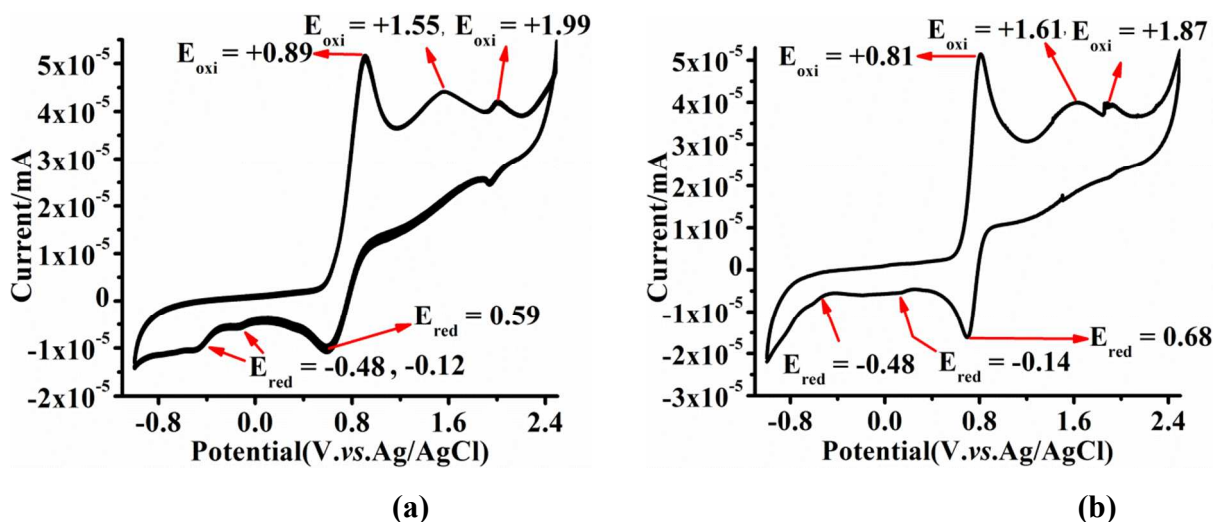E(triplet) for Hybrid **1** = ((1240/662) – (1240/699))/2 (eV) = -0.04 eV

E(triplet) for Hybrid **2** = ((1240/666) – (1240/690))/2 (eV) = -0.03 eV

According to the formula E(CS) = E(ox of por) – E(red of POM) (eV), the energy levels of the charge separated states for hybrids **1** and **2** are determined:

E(CS) for Hybrid **1** = [0.79-(-0.87)]V = 1.64 V = -1.64 (ev)

E(CS) for Hybrid **2** = [0.77-(-0.87)]V = 1.66 V = -1.66 (ev)

(a)   **(b)**

Figure S6. Cyclic voltammograms of hybrid **1** (a) and hybrid **2** (b) in DMF/CH$_3$CN (v/v = 1:1) (all the compounds have the concentrations of 1 mM in the presence of 0.1 M (*n*-Bu$_4$N)PF$_6$ as a supporting electrolyte.

It is found that in cyclic voltammograms of hybrid **1** and hybrid **2** the first two peaks are oxidation peaks of porphyrin molecular moiety and reduction occurs at [-0.48, -0.12] V and [-0.48, -0.14] V for vanadium and tungsten present in hybrids **1** and **2** respectively, while potentials are somewhat shifted (Figure S6) (Hou, Y.; Hill, C. L., Hydrolytically Stable Organic Triester Capped Polyoxometalates with Catalytic Oxygenation Activity of Formula [RC(CH$_2$O)

$_3V_3P_2W_{15}O_{59}]^{6-}$ (R = CH_3, NO_2, CH_2OH). *Journal of the American Chemical Society* **1993**, *115*, 11823-11830; Zonoz, F. M.; Aliabadi, F., A New Sandwich-Type Polyoxometalates Containing Mixed Transition Metals,$[Cd_2Zn_2(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$: Syntheses, Spectrochemical Characterization and Its Electrocatalytical Activity Comparison with $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$(M= Cd^{2+} and Zn^{2+}) and $[P_2W_{15}O_{56}]^{12-}$. *Inorganica Chimica Acta* **2016**, *444*, 87-94.).

Primary equations used to find the important parameters of third-order nonlinear optical properties.

Refractive index n_2 (esu), the nonlinear absorption coefficient β (esu) and the third-order optical nonlinear susceptibility $\chi^{(3)}$ (esu) are evaluated by the following formulae.[4]

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}|\Delta\varphi_0|,$$ (Equation S1)

$$\Delta\varphi_0 = kL_{eff}\gamma I_0,$$ (Equation S2)

$$L_{eff} = (1-e^{\alpha_0 L})/\alpha_0,$$ (Equation S3)

$$n_2(esu) = \frac{cn_0}{40\pi}\gamma \text{ (m}^2\text{/W)},$$ (Equation S4)

Where, ΔT_{P-V} is called as Normalized peak-valley difference, The symbol $\Delta\varphi_0$ is used for phase shift of the beam at the focus, $K = 2\pi/\lambda$ is named as wave vector, I_o (unit: W/m^2) is used to describe the intensity of the light at focus point, L_{eff} is used to represent the effective length of the sample measured in terms of the linear-absorption coefficient α_0 and the true optical path length through the sample, n_0 indicates the linear refractive index, and γ is called as optical Kerr constant. The conversion can be realized between n_2 (esu) and γ (m^2/W) by equation (S4).

Normalized transmittance $T(z, s = 1)$ can be expressed as

$$T(z, s=1) = \sum_{m=0}^{\infty}\frac{[q_0(z)]^m}{(m+1)^{3/2}},$$ (Equation S5)

When sample is measured under open aperture.

Where, $q_0(z) = \beta I_0 L_{eff}/(1+z^2/z_0^2)$, β is nonlinear absorption coefficient.

(β) Which is called as nonlinear absorption coefficient is determined by above given equation 5. Very important parameters like third-order optical nonlinear susceptibility Im$\chi^{(3)}$, Re$\chi^{(3)}$ and $\chi^{(3)}$ are calculated by using the following equations (S6-S8)

$\text{Im}\chi^{(3)} \text{ (esu)} = (n_0{}^2 c^2/240\,\pi^2\omega)\beta\text{(m/W)} = 100\lambda n_0\beta \text{ (esu)} / 6\pi^2$ (Equation S6)

$\text{Re}\chi^{(3)}\text{(esu)} = n_0{}^2 c\gamma\text{(m}^2\text{/w)}/120\pi^2 = n_0 n_2\text{(esu)}/3\pi$ (Equation S7)

$$\chi^{(3)} = \sqrt{\left(\frac{c n_0}{160\pi^2}\gamma\right)^2 + \left(\frac{c\beta n_0^3\lambda}{64\pi^3}\right)^2},$$ (Equation S8)

Equation S9[5] is the source to find out the molecular second hyperpolarizability γ of the samples

$$\gamma = \frac{\chi^{(3)}}{N_c L}.$$ (Equation S9)

where given symbols are used to denote the following parameters.

n_0 = Linear refractive index of sample.

N_c = Molecular number density per cubic centimeter.

L = Local-field correction factor, which may be approximated by $[(n_0{}^2+2)/3]^4$.[5]

References

1.   Hassan, S. U; Asif, H. M.; Zhou, Y.; Zhang, L.; Qu, N.; Li, J.; Shi, Z. "Closer Is Better and Two Is Superior to One": Third-Order Optical Nonlinearities of a Family of Porphyrin–Anderson Type Polyoxometalate Hybrid Compounds. *J. Phys. Chem. C.* **2016**. DOI: 10.1021/acs.jpcc.6b09951.

2.   Allain, C.; Schaming, D.; Karakostas, N.; Erard, M.; Gisselbrecht, J.-P.; Sorgues, S.; Lampre, I.; Ruhlmann, L.; Hasenknopf, B. Synthesis, Electrochemical and Photophysical Properties of Covalently Linked Porphyrin–Polyoxometalates. *Dalton Trans.* **2013**, *42*, 2745-2754.

3.   Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M., Rothemund and Adler-Longo Reactions Revisited: Synthesis of Tetraphenylporphyrins under Equilibrium Conditions. *J. Org. Chem.* **1987**, *52*, 827-836.

4.   Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; Van Stryland, E. W. Sensitive Measurement of Optical Nonlinearities Using a Single Beam. *IEEE Journal of Quantum Electronics.* **1990**, *26*, 760-769.

5.   Wang, S.; Huang, W.; Zhang, T.; Yang, H.; Gong, Q.; Okuma, Y.; Horikiri, M.; Miura, Y. F. Third-Order Nonlinear Optical Properties of Didodecyldimethylammonium-Au (dmit)~ 2. *Appl. Phys. Lett.* **1999**, *75*.