

# Non-porous Interpenetrating Co-bpe MOF for colorimetric iodide sensing

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## Supporting information

### Other Physical Measurements:

The Single crystal XRD analysis were carried out on a BRUKER AXS SMARTAPEX diffractometer with a CCD area detector (MoK $\alpha$  = 0.71073 Å, monochromator: graphite).<sup>[1]</sup> Frames were collected at T = 293 corrected for absorption with SADABS.<sup>[2]</sup> Structure solution, refinement, and data output were carried out with the SHELXTL program.<sup>[3]</sup> Non-hydrogen atoms were refined anisotropically. C-H and N-H hydrogen atoms were placed in geometrically calculated positions by using a riding model. O-H hydrogen atoms of organic ligand were localized by difference Fourier maps and refined in subsequent refinement cycles. Hydrogen atoms on cluster oxygens could not be located. Images were created with the Diamond program.<sup>[4]</sup> Hydrogen bonding interactions in the crystal lattice were calculated with SHELXTL and Diamond. <sup>[3,4]</sup>

Powder X-ray diffraction analysis were carried out on a Bruker D8 Eco Diffractometer using Ni-filtered Cu K $\alpha$  radiation at room temperature. The data were collected over the range of  $2^\circ < 2\theta < 80^\circ$  with a step size of  $0.01^\circ$ . The surface morphology was explored by Scanning electron microscopy (SEM) on a JEOL JSM-6100 system. The BET nitrogen isotherm analysis was

carried out on Quantachrome ASiQwin at 300K. UV/Vis spectrophotometer (Shimadzu UV-2600) was used for Diffusion reflectance spectroscopy (DRS). Solid state photoluminescence (PL) was analyzed on Fluorolog 3-221 (Horiba Scientific). NMR spectra was recorded on BRUKER 400 MHz. The X-ray photoelectron spectroscopy (XPS) was carried out on Thermofischer scientific (Model: NEXSA base) with a micro-focused (400 $\mu$ m, 72 W, 12000 V) monochromatic Al-K $\alpha$  source ( $h\nu = 1486.6$  eV), a hemispherical analyser and a 128 channel plate detector.

**Table S1:** Crystallographic parameters of Co-*bpe*

Parameters	$\text{Co}_2(\text{bpe})_{2.5}(\text{NO}_3)_4(\text{CH}_3\text{O})$
Formula	$\text{C}_{31} \text{H}_{28} \text{Co}_2 \text{N}_9 \text{O}_{13}$
Formula weight (g)	852.48
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 21/c (No.14)
a (Å)	13.471(3)
b (Å)	15.430(3)
c (Å)	17.434(4)
$\alpha$ (°)	90.00
$\beta$ (°)	90.00(3)
$\gamma$ (°)	90.00
V (Å <sup>3</sup> )	3623.8 (14)
Z	4
dcalc (gcm <sup>-3</sup> )	1.563
$\mu_{\text{MoK}\alpha}$ (cm <sup>-1</sup> )	0.993
Data ( $I > 2\sigma I$ )	3597
WR2(all)	0.1047
F(000)	1740
$\theta_{\text{min}}$ (deg)	2.0
$\theta_{\text{max}}$ (deg)	28.7
no. of total data	39312
no. of unique data	5479
R(int)	0.100
R1 <sup>a</sup>	0.0383
wR2	0.1047
S	1.04

CCDC No.	2063799
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**Table S2**– The selected Hydrogen Bonds (Å,°)

D--H---A	D---H	H---A	D---A	D-H---A
C1-- H1--O2	0.9300	2.5600	3.233(6)	130.00
C10-- H10--O9	0.9300	2.4800	3.053(5)	120.00
C12-- H12--N3	0.9300	2.3900	2.982(4)	121.00
C13-- H13--O8	0.9300	2.3300	2.921(4)	121.00
C17-- H17--O10	0.9300	2.3700	3.179(4)	145.00 <sup>i</sup>
C24-- H24--O11	0.9300	2.4700	3.373(5)	162.00 <sup>ii</sup>
C27--H27--O10	0.9300	2.5600	3.239(5)	131.00 <sup>iii</sup>
C29--H29C--O6	0.9600	2.5500	3.480(8)	165.00 <sup>iv</sup>
C31--H31--O5	0.9300	2.6000	3.201(6)	123.00

Symmetry codes: (i) 1-x,-1/2+y,1/2-z, (ii) 1-x,-y,-z, (iii) x,1/2-y,-1/2+z, (iv) 2-x,2-y,1-z

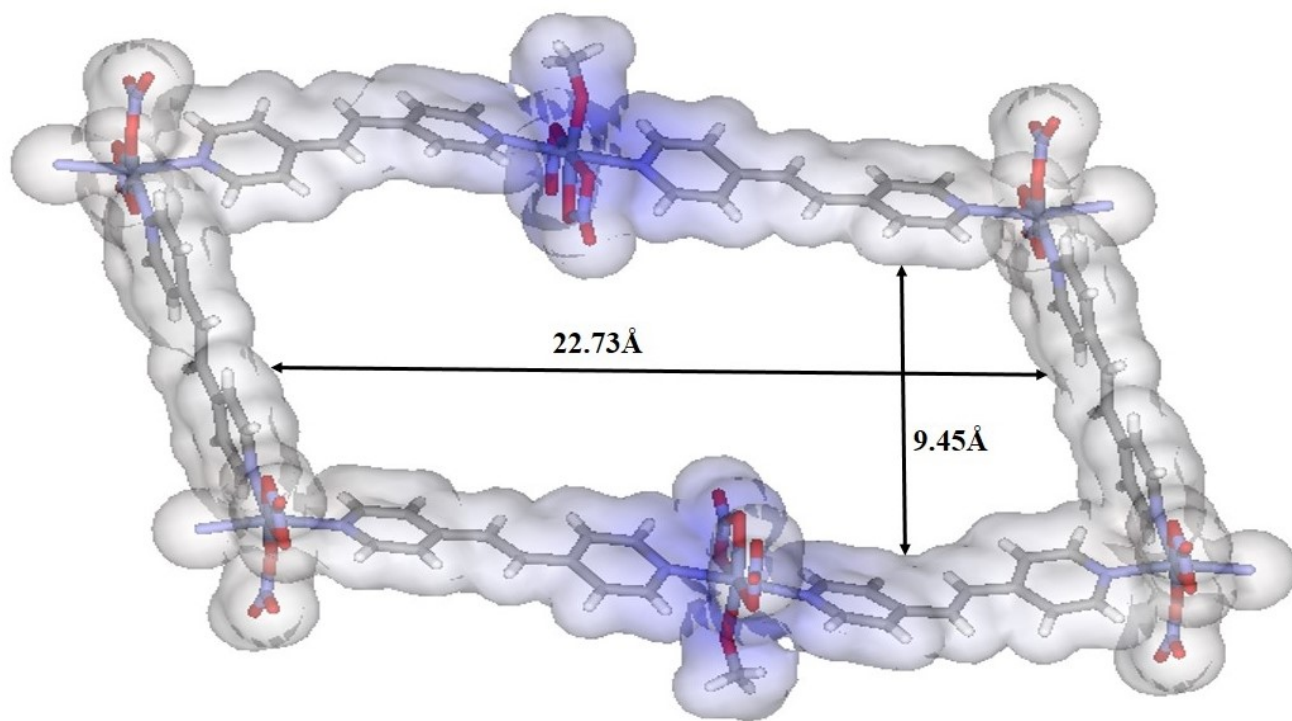
**Table S3**– Bond valence for Co1 and Co2.

	Bond length (Å)	Bond valence
Co1 -O8	2.174 (3)	0.272
Co1 -O9	2.147(3)	0.292
Co1 -O13	2.116(3)	0.318
Co1 -N2	2.082(3)	0.454
Co1 -N3	2.195(3)	0.334
Co1 -N4	2.165(3)	0.363
	<b>Valence Sum</b>	<b>2.033</b>
Co2 -O1	2.303(3)	0.192
Co2 -O2	2.129(3)	0.307
Co2 -O4	2.515(3)	0.108
Co2 -O5	2.036(3)	0.395
Co2 -O7	2.164(3)	0.279
Co2 -N1	2.206(3)	0.324
Co2 -N5	2.192(3)	0.337
	<b>Valence Sum</b>	<b>1.942</b>

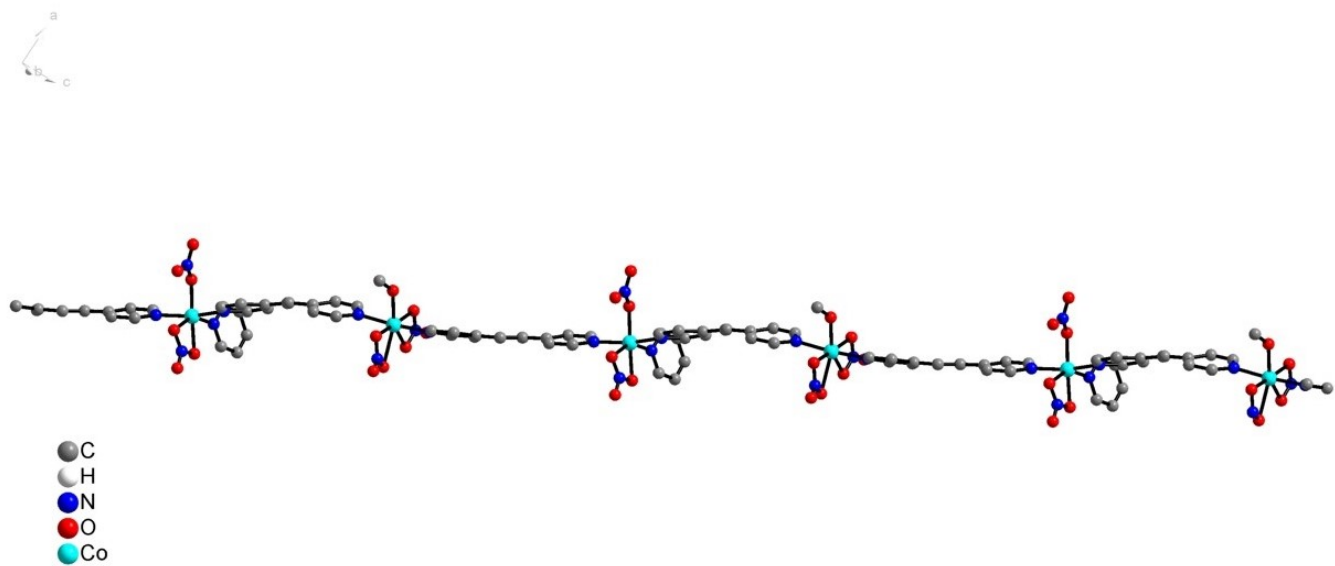
**Topological description of Co-bpe:**

The topological studies suggest that the overall structure is 2,3-c net with stoichiometry (2-c)(3-c) (Fig. 3,4). It is elucidated that the network is 2-nodal net where Co1 atom connected by bridging ligands and shares common vertex with Co2, Co2 and Co1 atoms and acts as acts as three connecting (3-c) whereas Co2 is also linked to bridging moieties and has common vertex with Co1 and Co1 and serve as a two-connecting node (2-c). The framework exhibits inclined

polycatenation and comprised of chains oriented in different plane  $[111]$  and  $[1-11]$  which shows self-crossovers. The two inclined 1D ladder shaped chains have dihedral angle  $70^\circ$  and the planes cross through the line  $[10-1]$ . There are four possible ring links in the structure and all are Hopf links. The point symbol and point symbol with loops of Co1 is  $\{6^2, 10\}$  and  $\{4^{2.6}\}$  respectively. Similarly, the point symbol of Co2 is  $\{6\}$  whereas the point symbol with loops is found to be  $\{4\}$ .

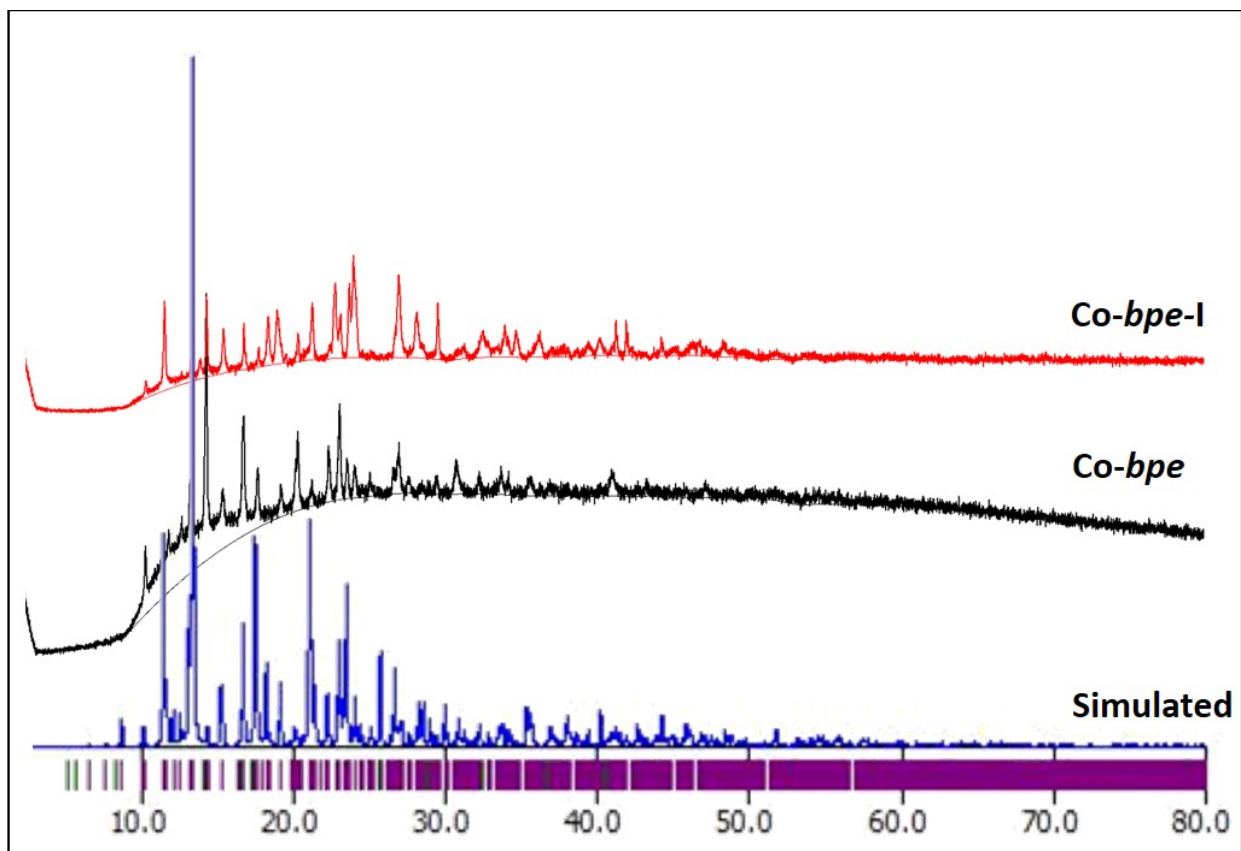


**Figure S1.** Void space between each rectangular channel

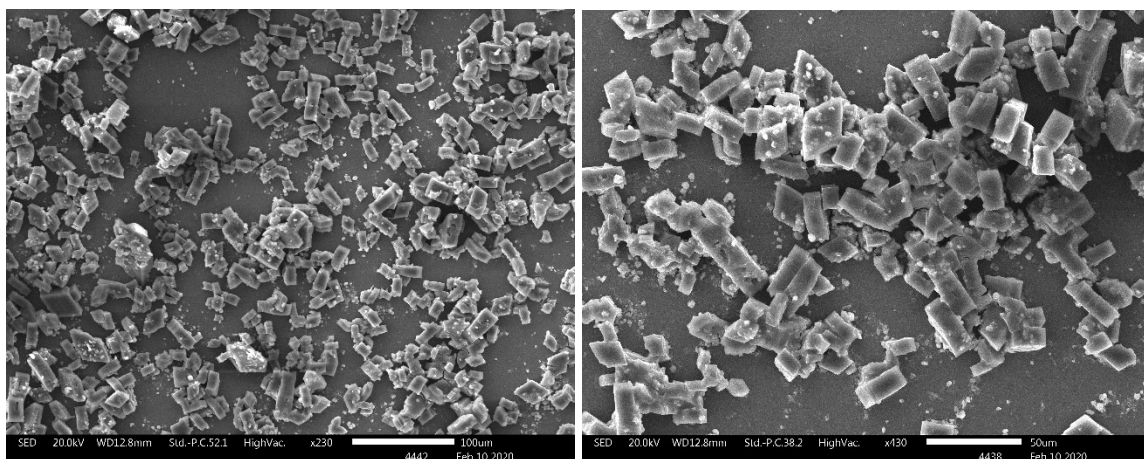


**Figure S2.** Molecular orientation along the chain of ladder





**Figure S3.** Powder XRD spectra of simulated, bulk and after iodide sensing of *Co-bpe*



**Figure S4.** SEM images of *Co-bpe*

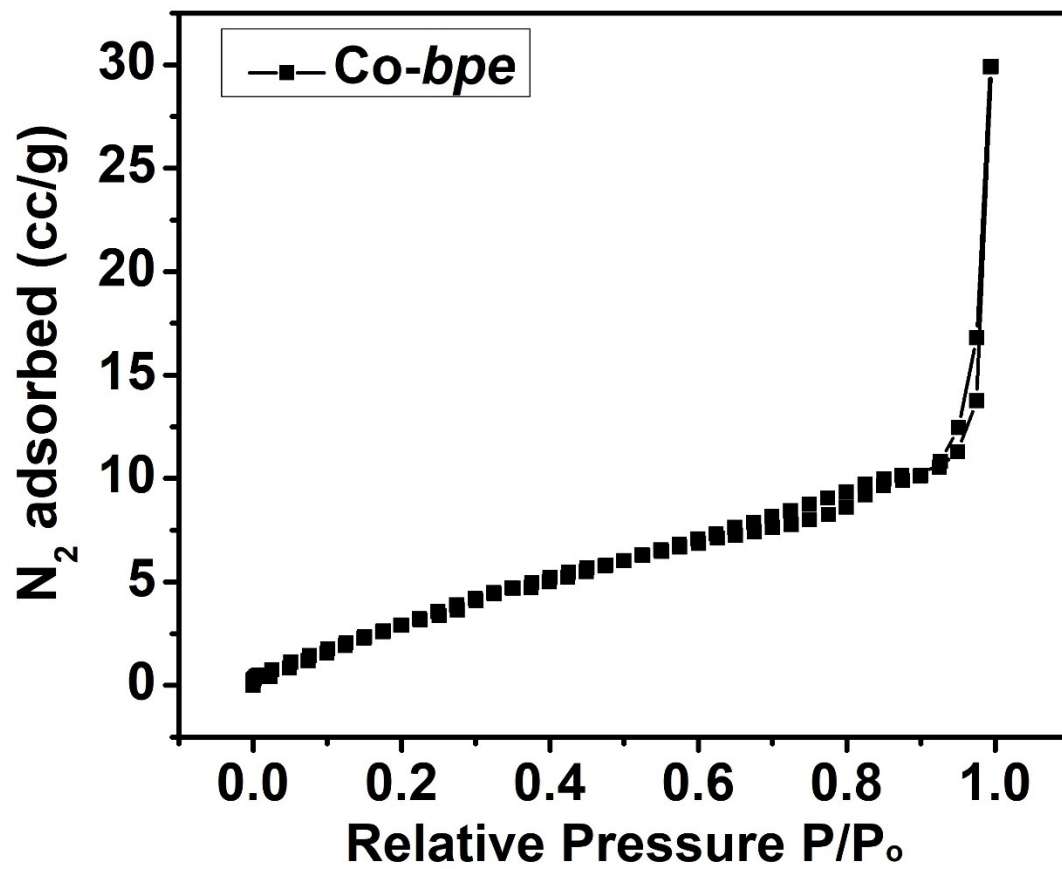
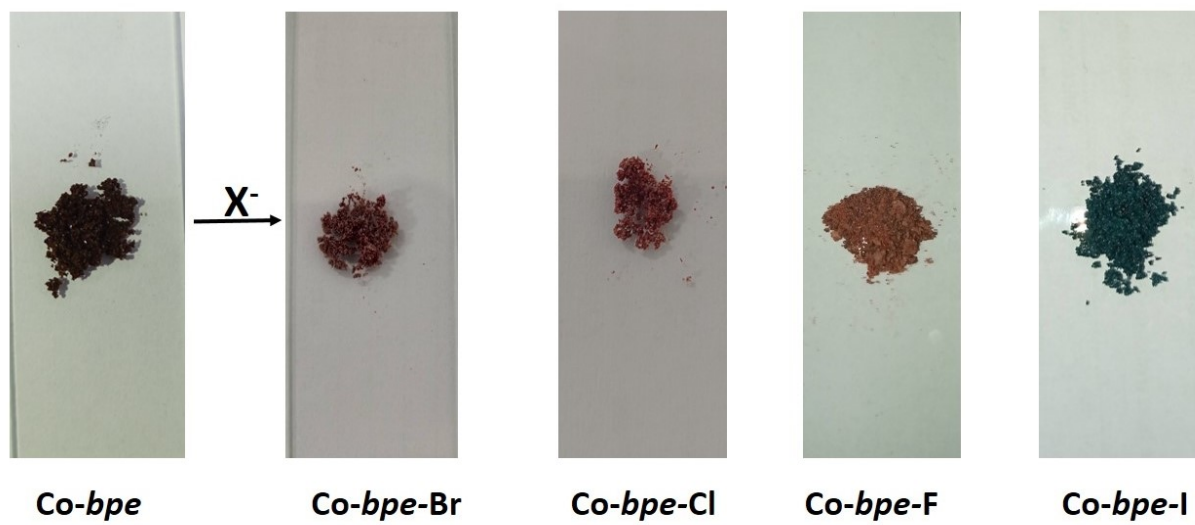


Figure S5. N<sub>2</sub> adsorption Isotherm of Co-bpe at 77K.



**Figure S6.** Chromic effect of Co-*bpe* under different halide solutions

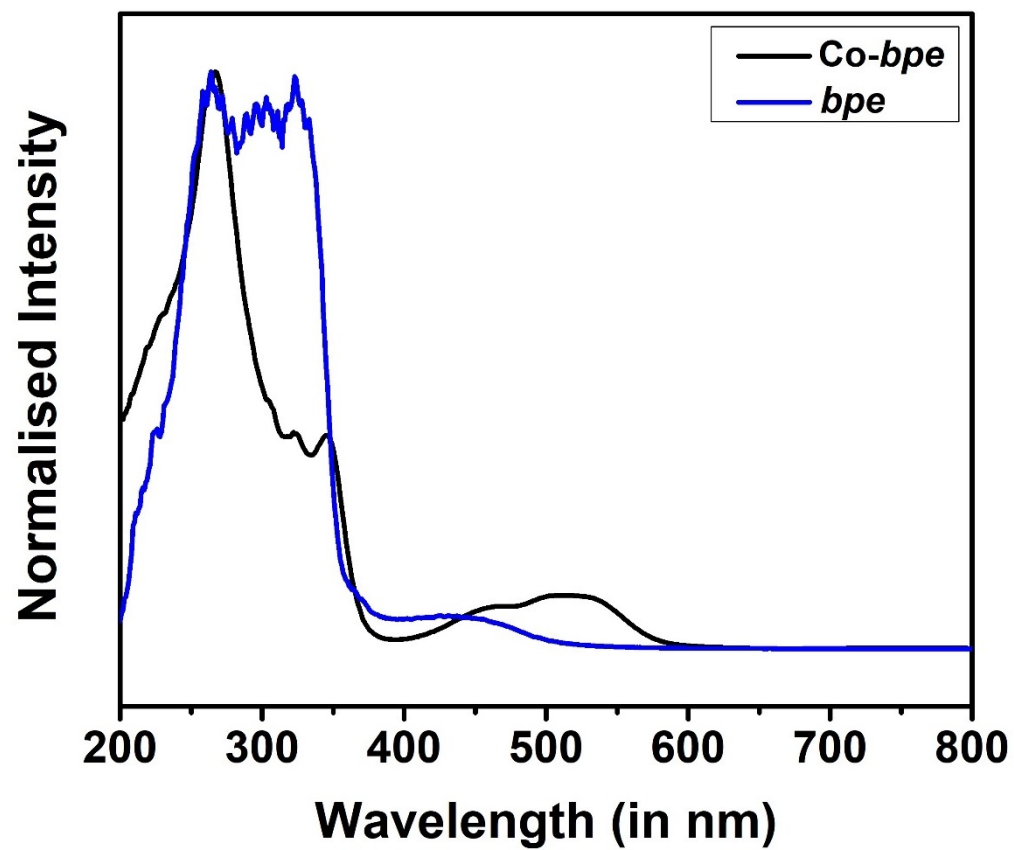


Figure S7. UV-Vis spectra of *bpe* and *Co-bpe*.

The optical properties was studied by calculating band gap using diffuse reflectance spectroscopy, where BaSO<sub>4</sub> is taken as reference. The following equation is used to calculate band gap (E<sub>g</sub>):

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

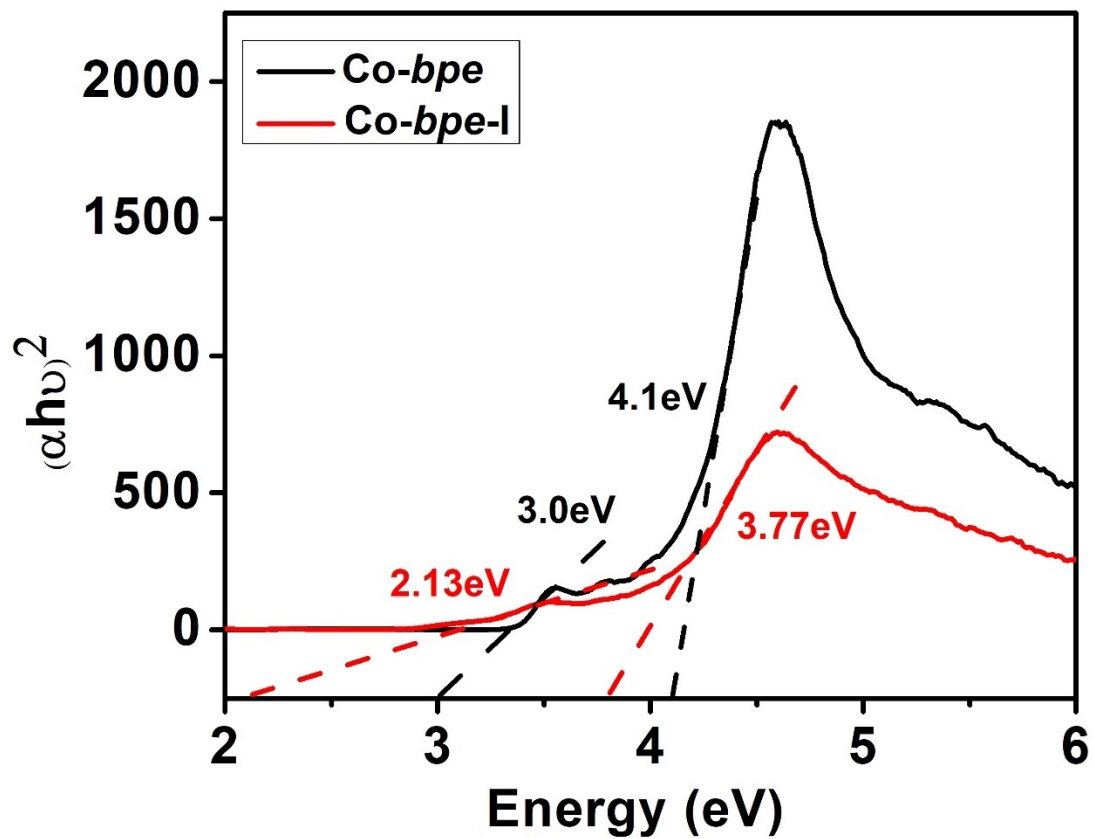
where,  $\alpha$  signifies absorption coefficient,  $h\nu$  and A denotes discrete photon energy and a constant relative to the material, respectively. The relation of absorption coefficient ( $\alpha$ ) to Kubelka-Munk function as follows:

$$F(R) = (1-R)^2 / 2R = \alpha/S \quad (2)$$

$$R = R_{\text{sample}} / R_{\text{BaSO}_4} \quad (3)$$

where, F(R), R, and S represents the Kubelka-Munk function, reflectance and scattering coefficient, respectively. Therefore, the band gap for Co-*bpe* and Co-*bpe*-I can be calculated from the plot of (F(R)  $h\nu$ )<sup>2</sup> vs  $h\nu$  (Tauc Plot) by extrapolating the linear regime of the resulting curves to F(R) = 0.

Herein, Co-*bpe* shows two energy band gaps of 4.1 and 3.0 eV whereas, Co-*bpe*-I displays band gaps at 3.77 and 2.13 eV. (Figure S8)



**Figure S8.** Tauc Plot: Band gap of Co-bpe and Co-bpe-I.

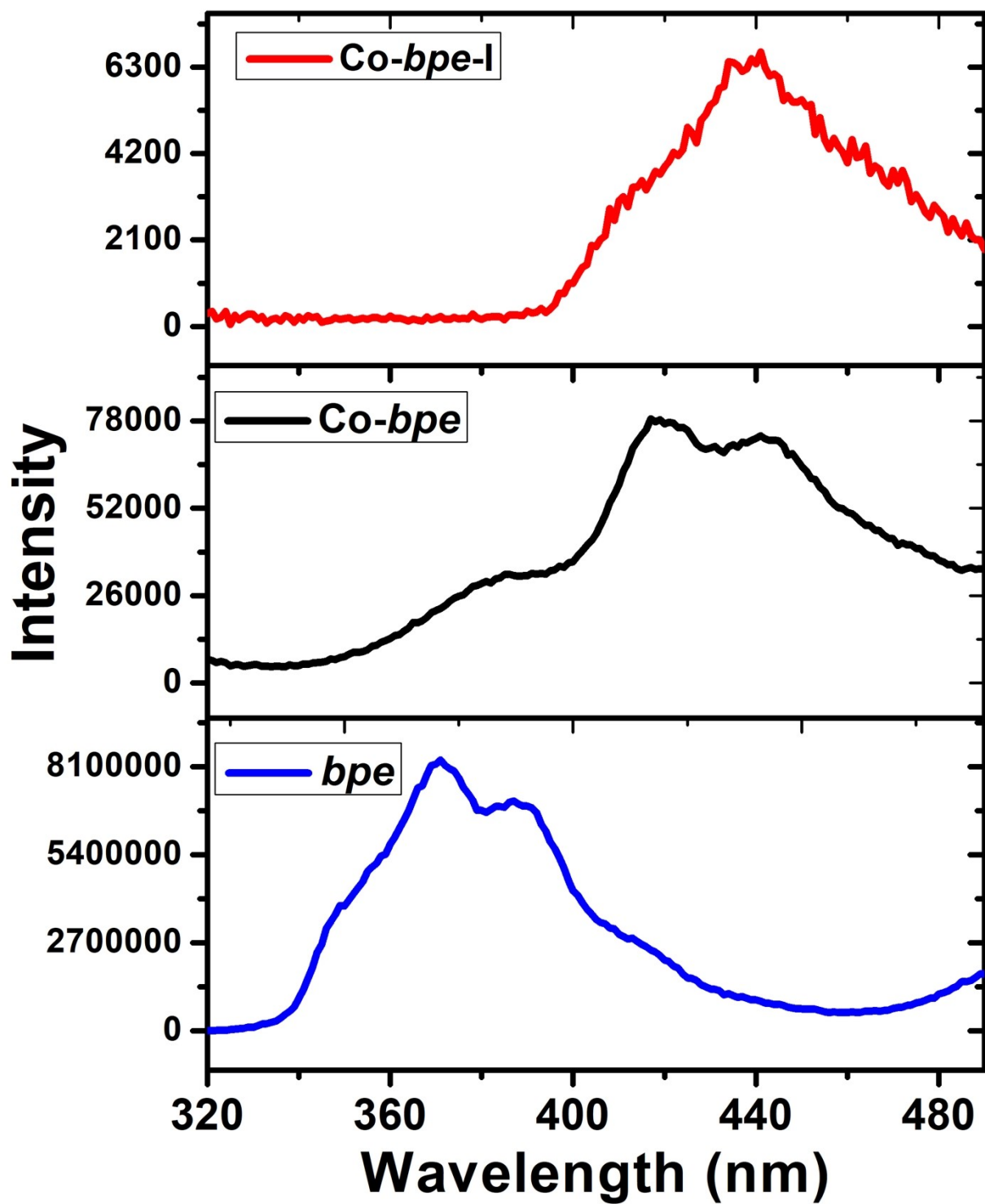


Figure S9. Photoluminescence spectra of *Co-bpe*, *Co-bpe-I* and *bpe*.



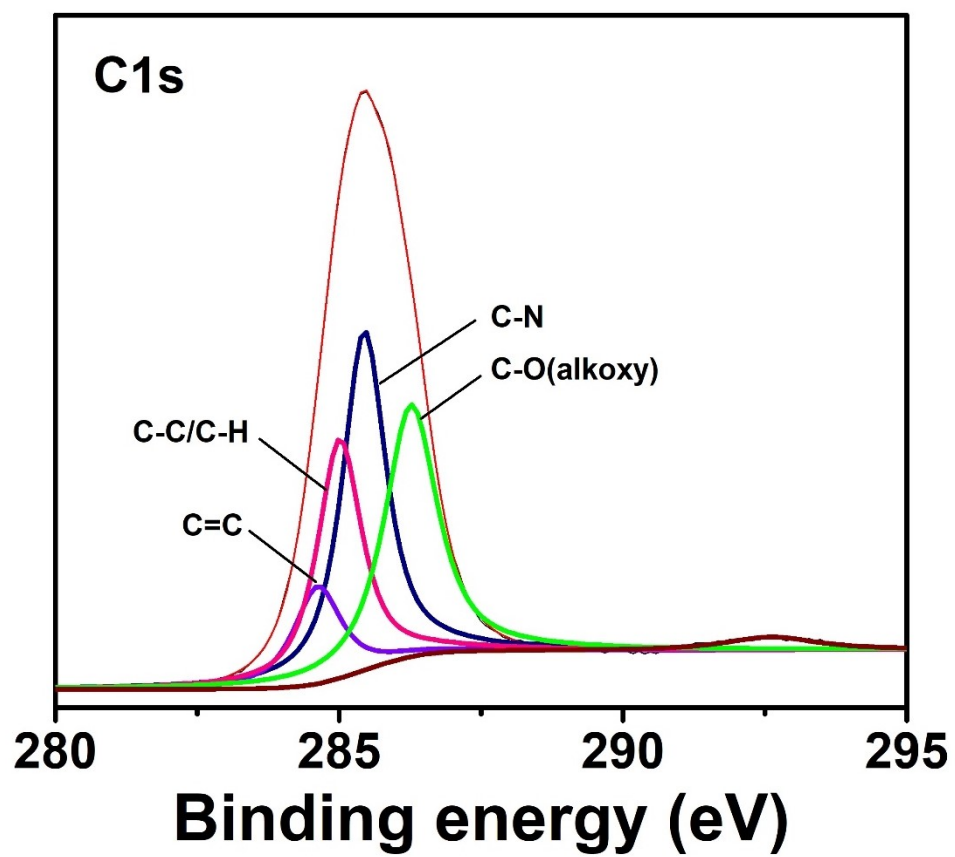


Figure S10. XPS spectra of C1s of Co-*bpe* .

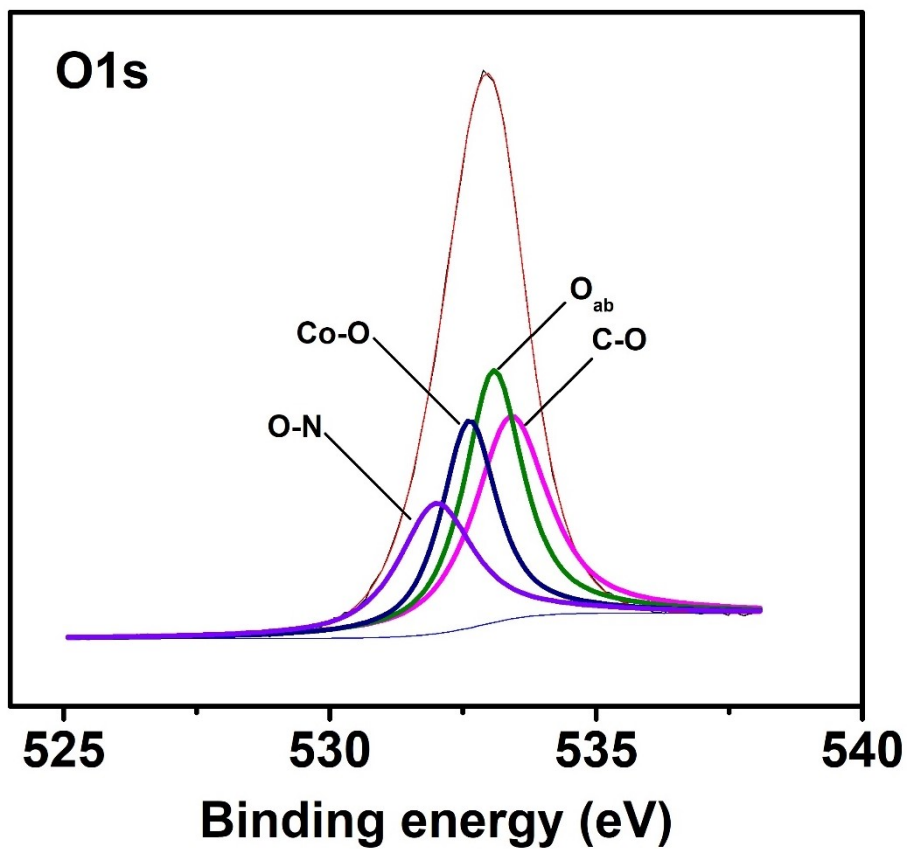


Figure S11. XPS spectra of O1s of Co-*bpe* .

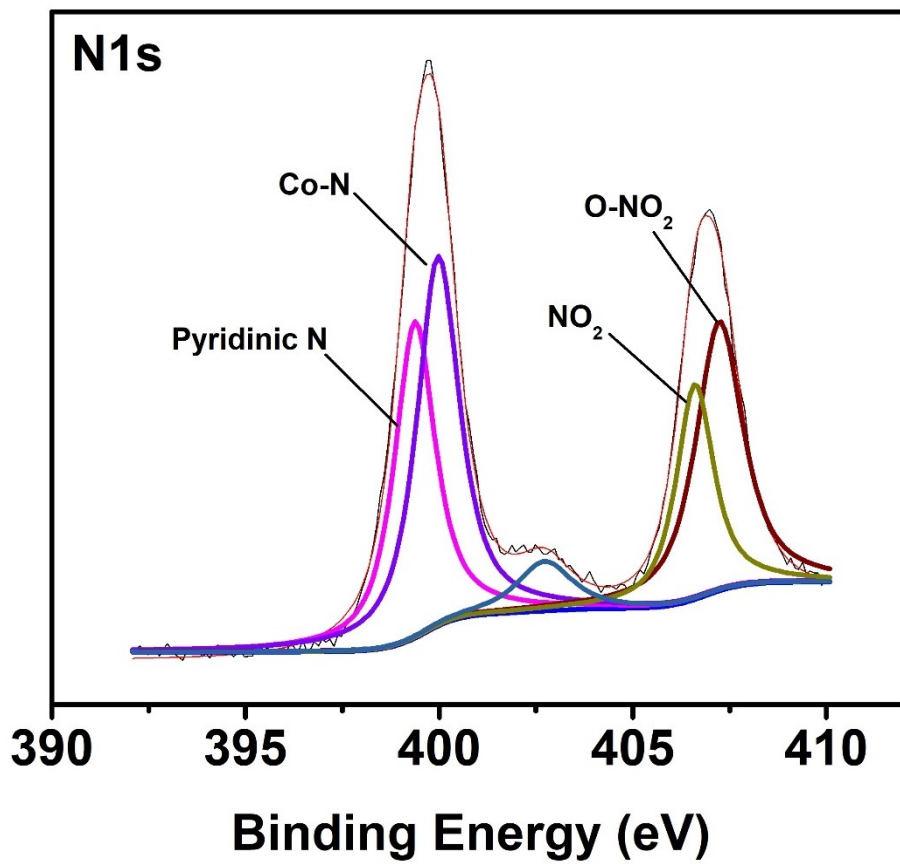


Figure S12. XPS spectra of N1s of Co-*bpe* .

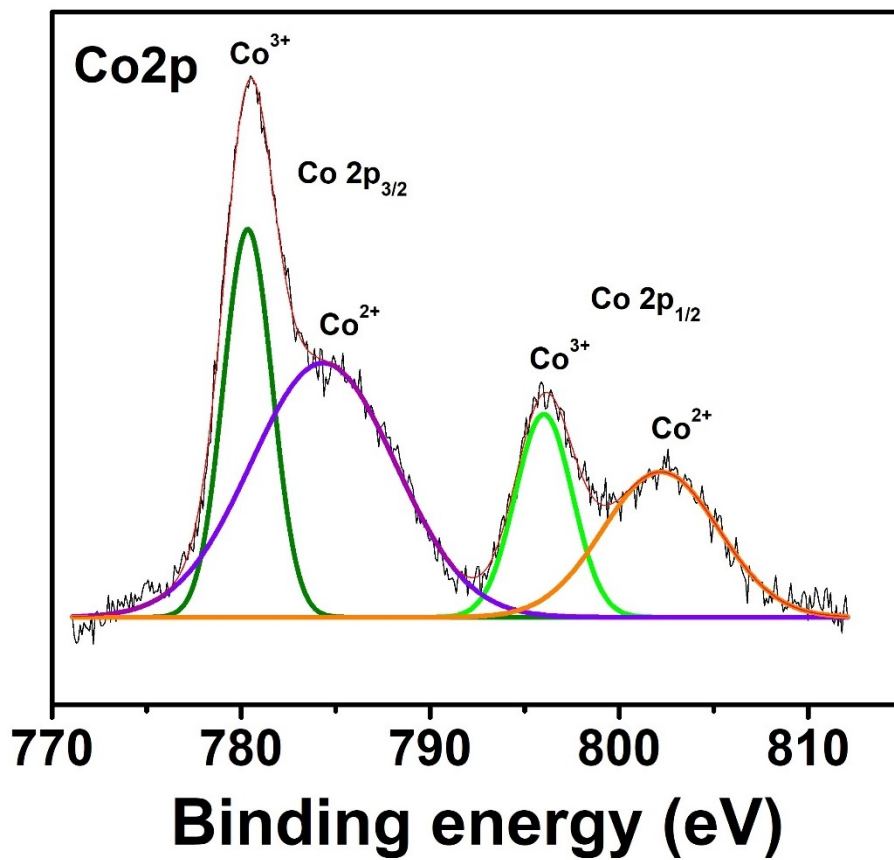
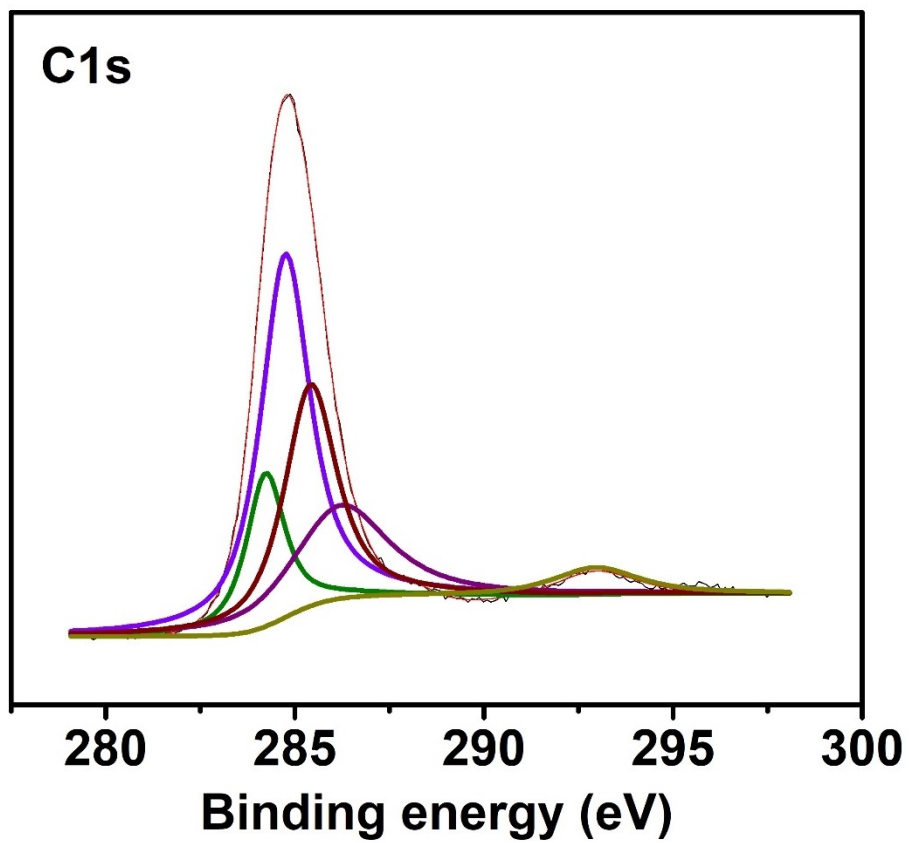


Figure S13. XPS spectra of Co<sub>2</sub>P of Co-*bpe*-I.



**Figure S14.** XPS spectra of C1s of Co-*bpe*-I.

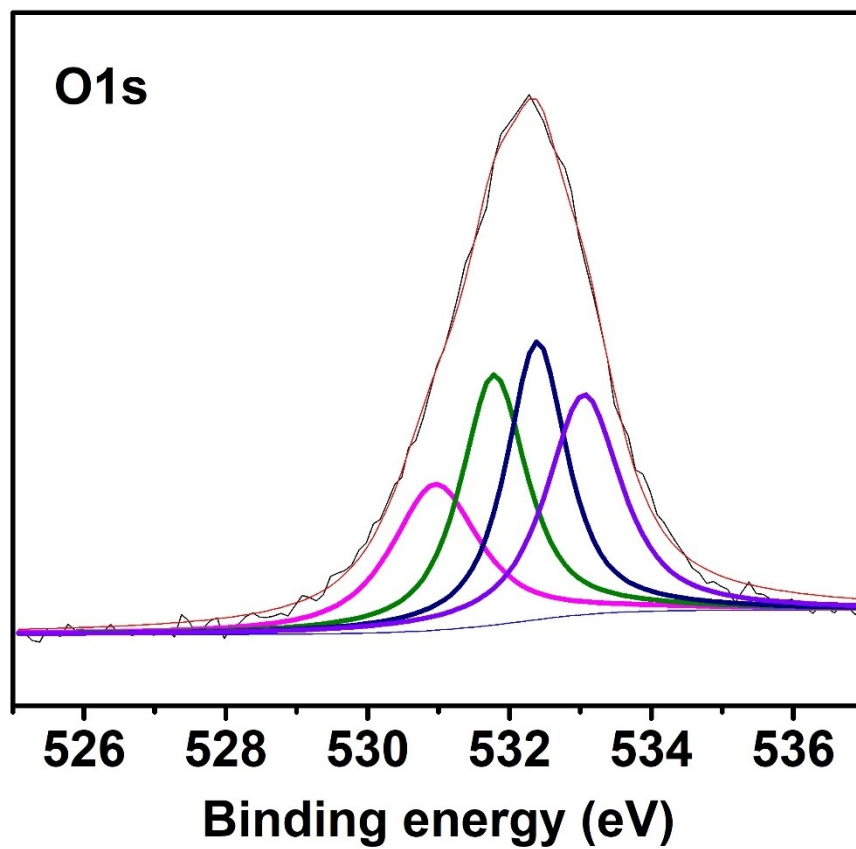
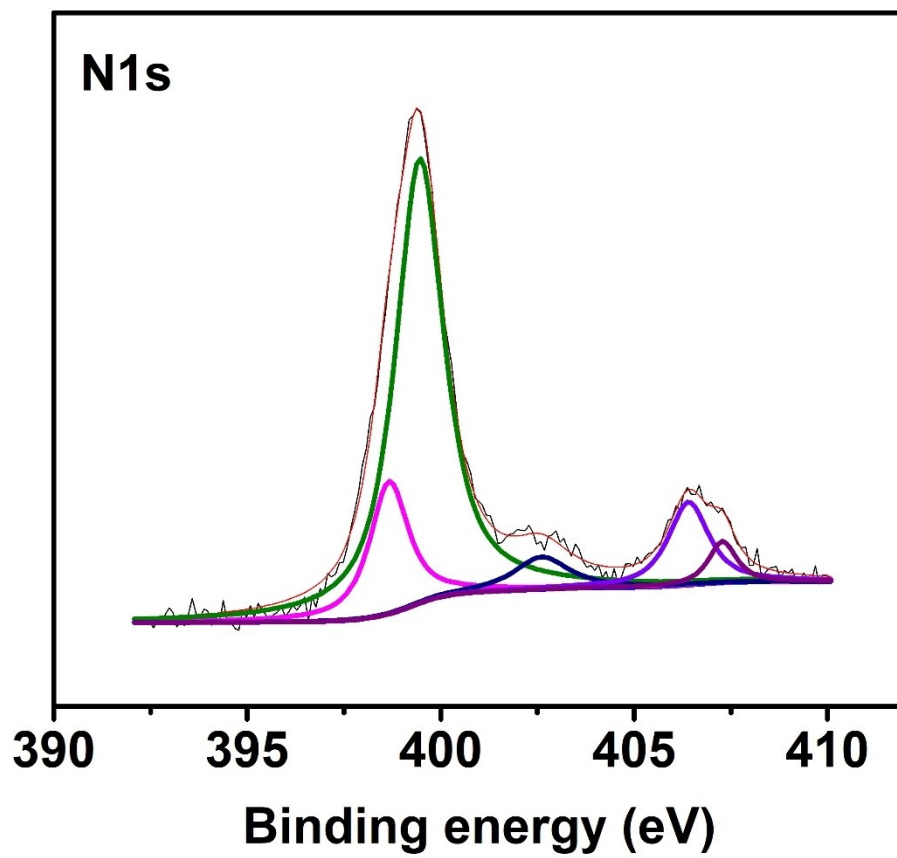


Figure S15. XPS spectra of O1s of Co-*bpe*-I.



**Figure S16.** XPS spectra of N1s of Co-*bpe*-I.

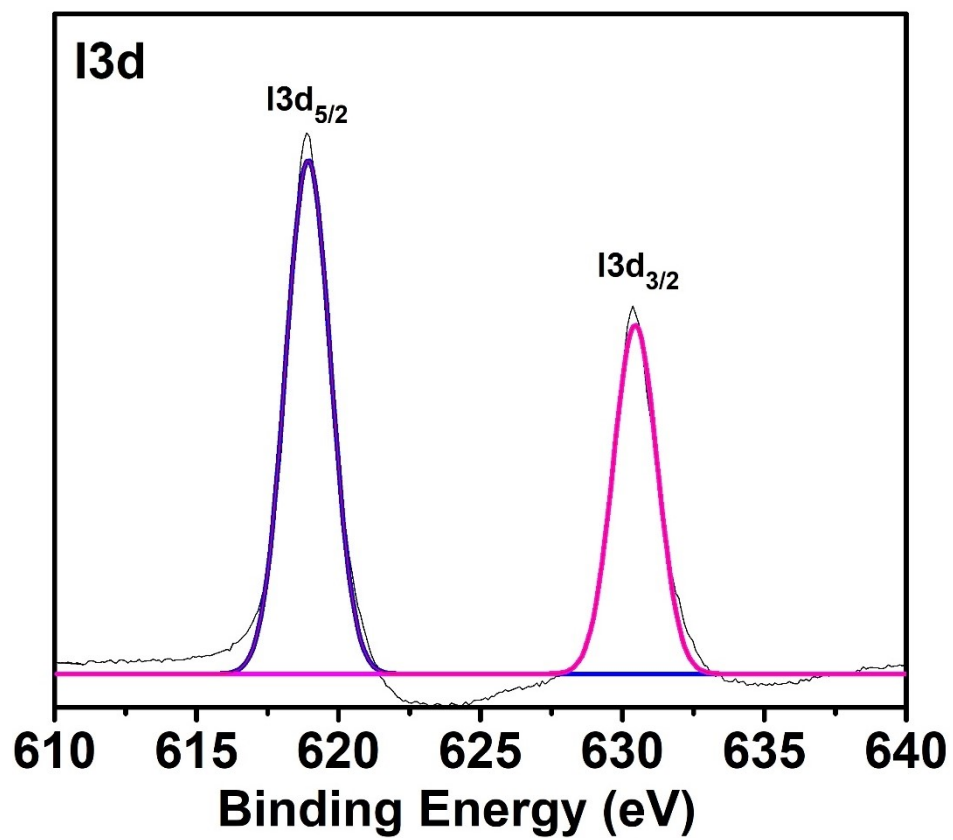


Figure S17. XPS spectra of I3d of Co-bpe-I.

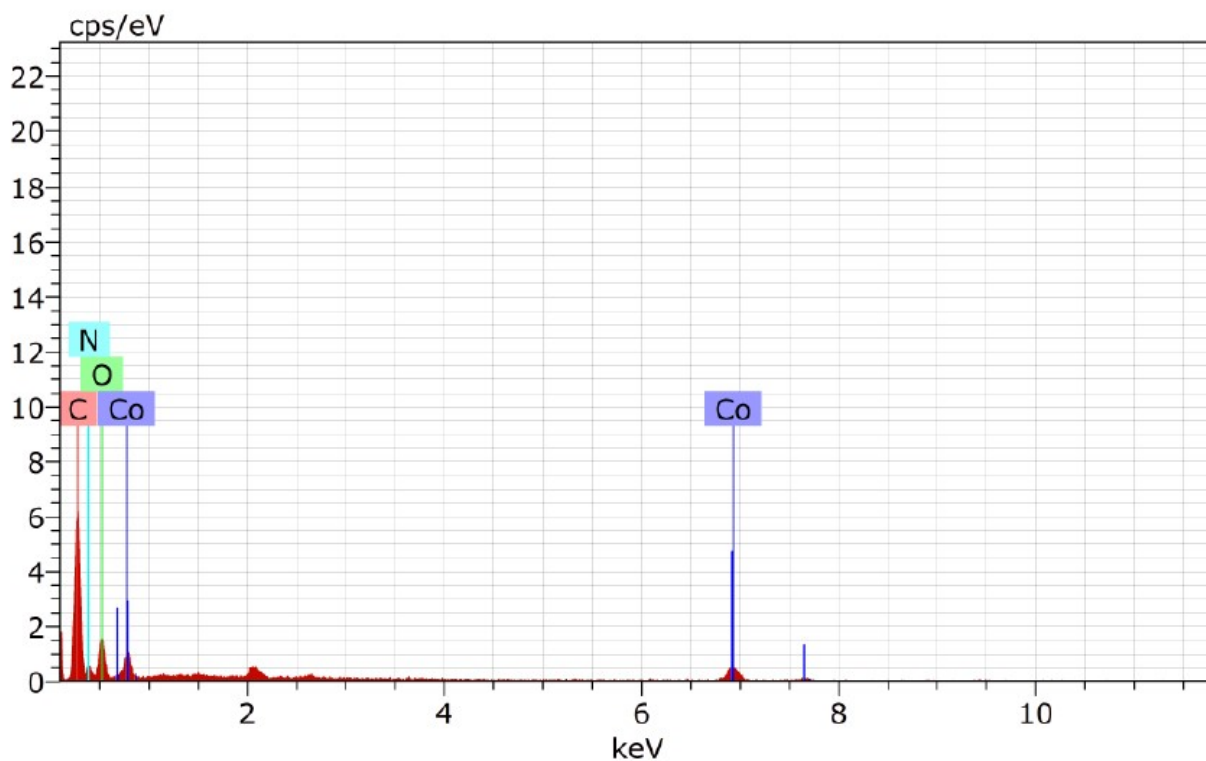


**Table S4** XPS quantification of peaks of *Co-bpe*

<b>Peak Name</b>	<b>Peak BE</b>	<b>FWHM eV</b>	<b>Area (P) CPS.eV</b>	<b>Atomic %</b>
C1s	285.91	3.03	782167.43	56.92
O1s	533.1	3.05	707617.39	21.31
N1s	400.17	2.94	361345.96	16.94
Co2p	782.14	4.01	812626.14	4.84

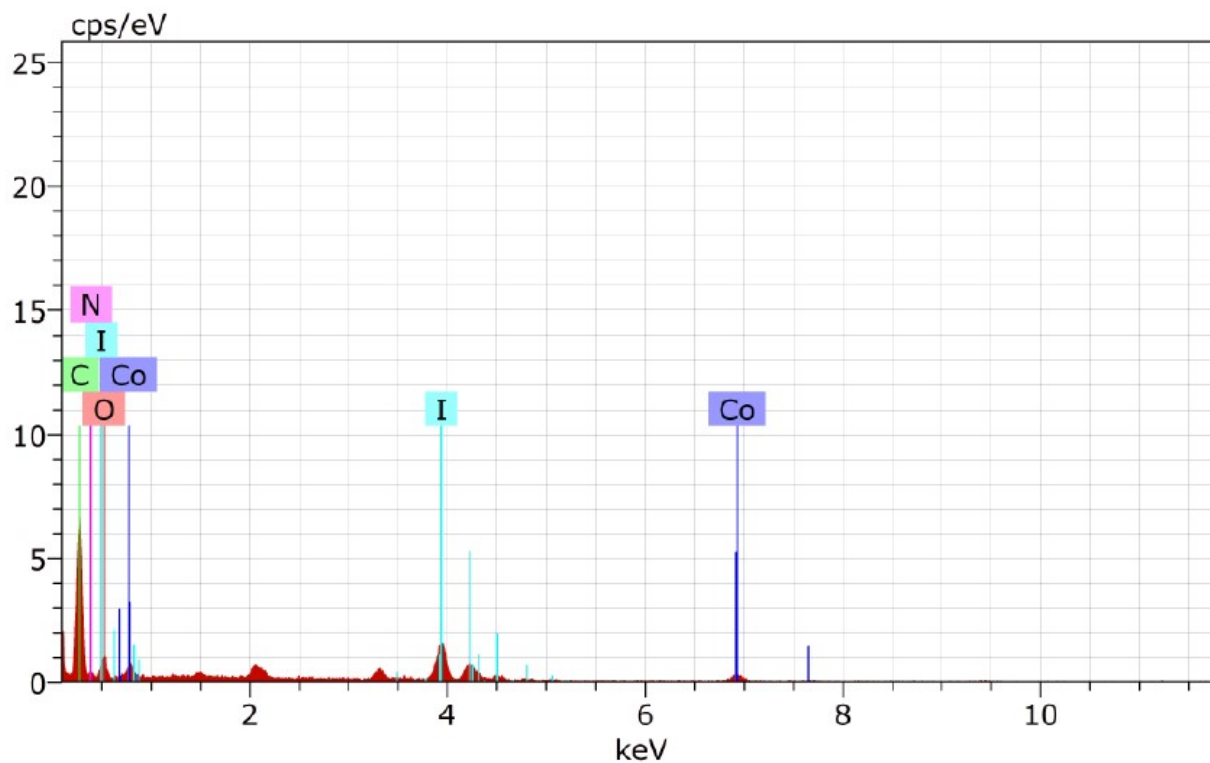
**Table S5** XPS quantification of peaks of Co-*bpe*-I

<b>Peak Name</b>	<b>Peak BE</b>	<b>FWHM eV</b>	<b>Area (P) CPS.eV</b>	<b>Atomic %</b>
C1s	285.05	3.01	684679.34	71.03
N1s	399.29	2.94	151601.68	10.13
O1s	532.15	3.36	201028.25	8.63
l3d	619.14	3	1673681.3	5.24
Co2p	781.21	5.33	584878.65	4.97



**Table S6.** EDX of Co-bpe

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	45.29	46.40	58.21	19.41
Oxygen	K-series	21.17	21.69	20.42	11.60
Cobalt	K-series	15.43	15.81	4.04	1.95
Nitrogen	K-series	15.72	16.10	17.32	11.33
Total:		97.61	100.00	100.00	



**Table S7.** EDX of Co-*bpe*-I

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Oxygen	K-series	4.88	6.80	9.17	3.14
Carbon	K-series	27.21	37.94	68.16	11.42
Cobalt	K-series	9.22	12.85	4.71	1.35
Iodine	L-series	24.78	34.56	5.88	2.45
Nitrogen	K-series	5.62	7.84	12.08	4.33
Total:		71.70	100.00	100.00	

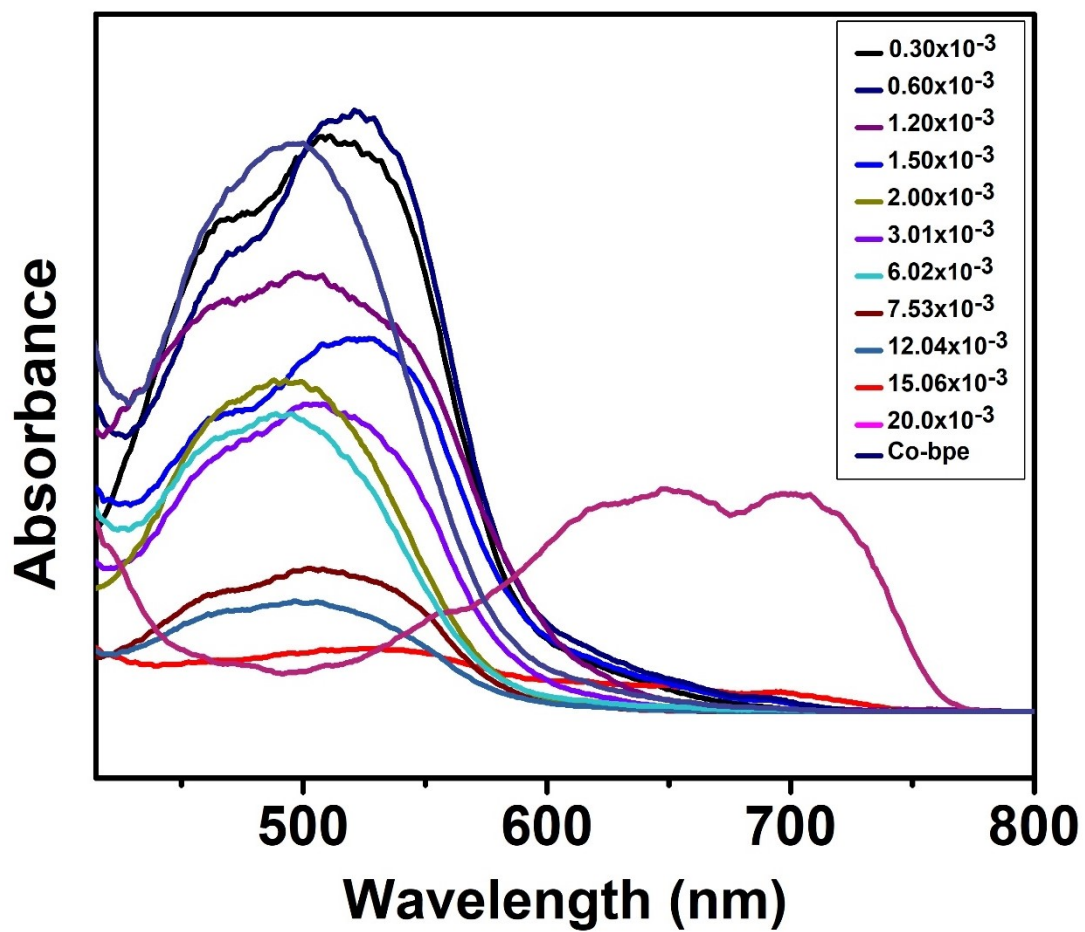
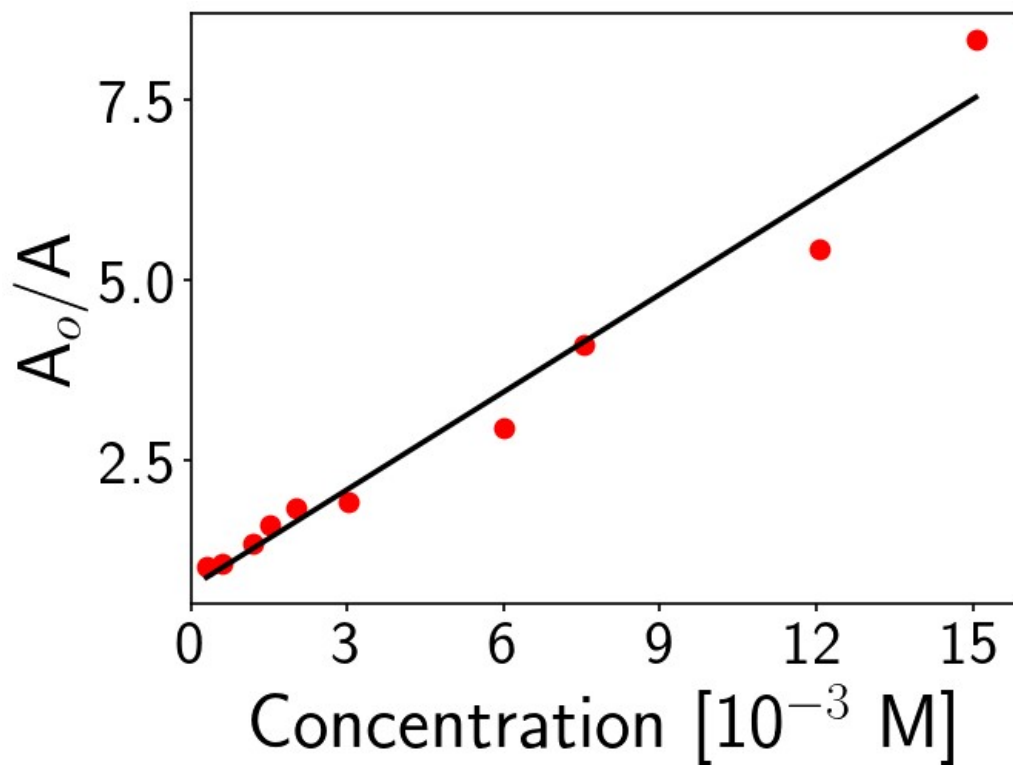


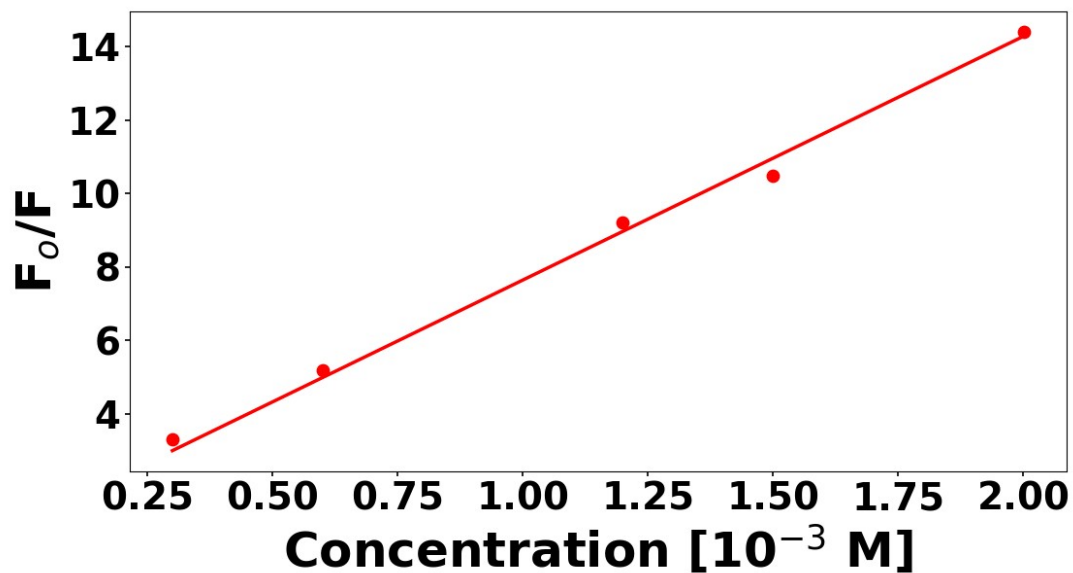
Figure S18. UV spectra of Co-bpe-I at different concentration of KI



**Figure S19.** Calibration curve obtained from UV-Vis spectra to find out the limit of detection of Co-*bpe* for iodide sensing.

$$R^2=0.997$$

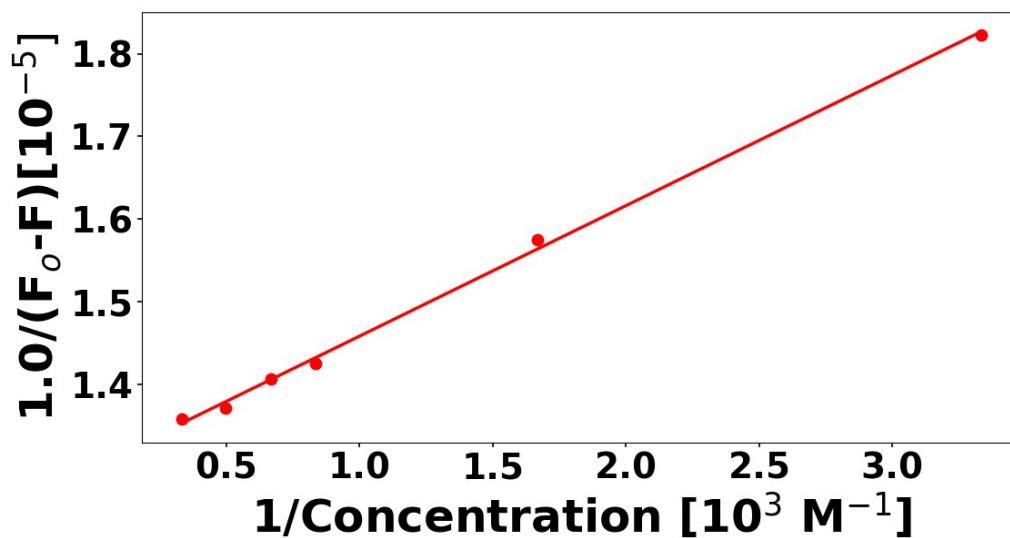
$$y= 424.93x + 1$$



**Figure S20.** Intensity versus concentration calibration curve to find out the limit of detection of *Co-bpe* for iodide sensing.

$$R^2=0.998$$

$$y= 6642.02x + 1$$



**Figure S21:** Benesi-Hildebrand plot

$$R^2 = 0.999$$

$$K_a = 13\text{M}^{-1}$$

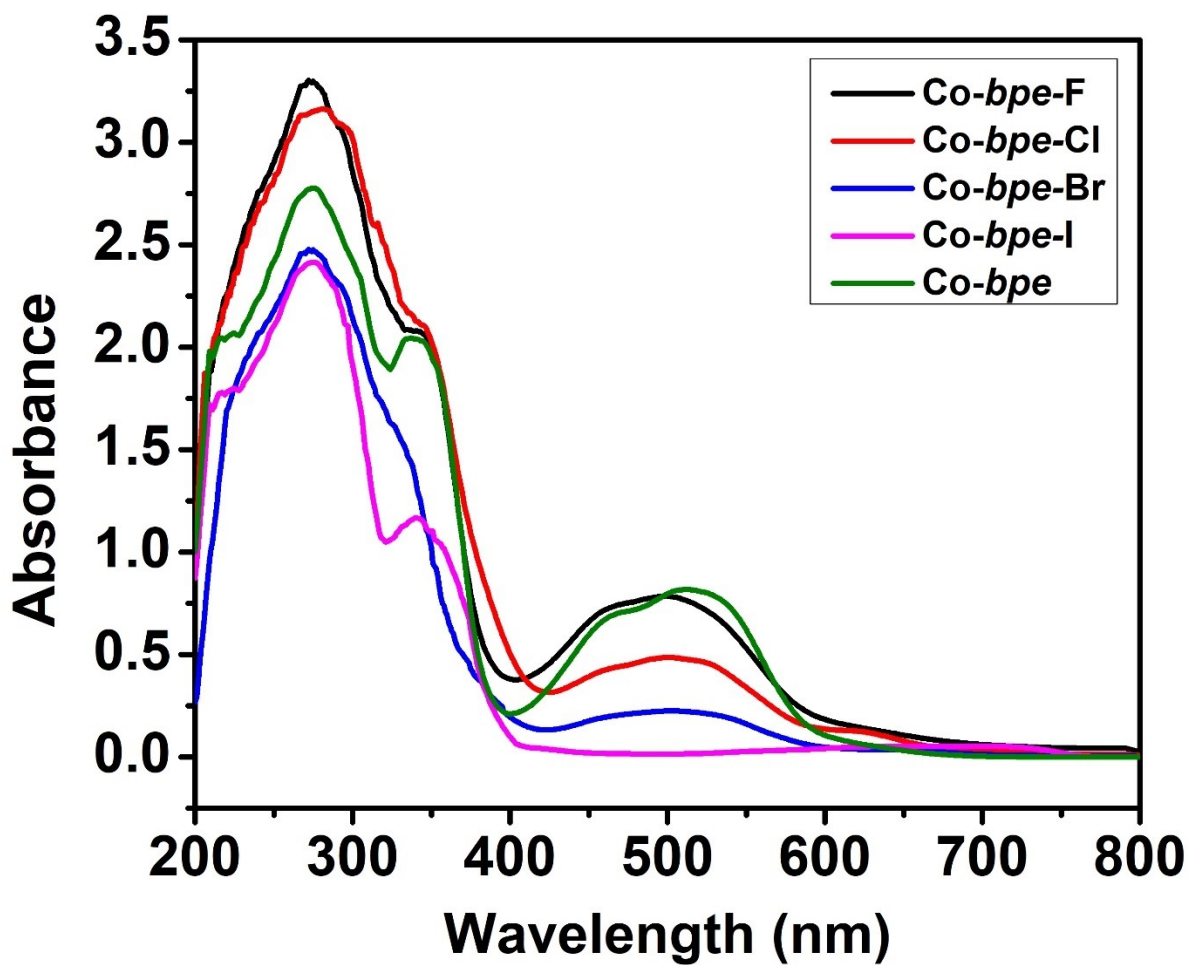


Figure S22. UV-Vis spectra of Co-bpe-I, Co-bpe-Br, Co-bpe-Cl, Co-bpe-F



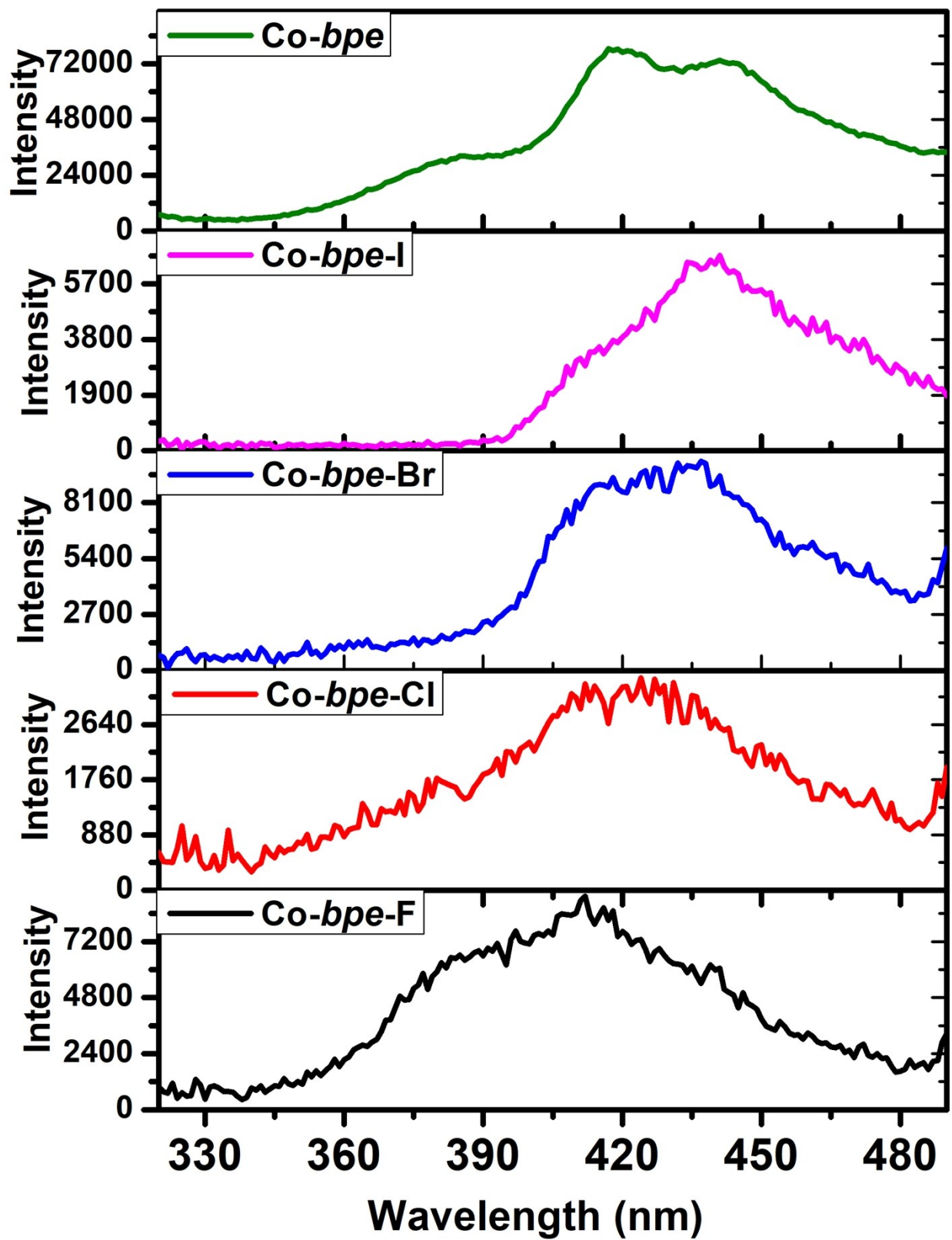
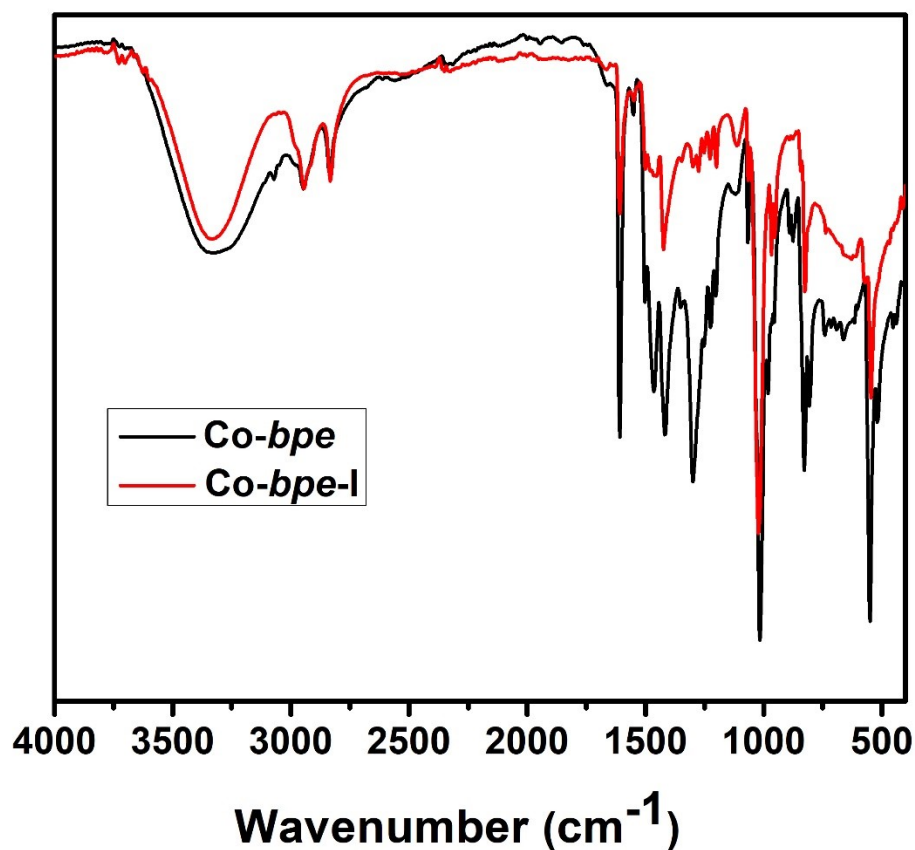


Figure S23. PL spectra of Co-bpe-I, Co-bpe-Br, Co-bpe-Cl, Co-bpe-F



**Figure S24.** FTIR spectra of *Co-bpe* and *Co-bpe-I*

**Reference:**

- [1].*Bruker Analytical X-ray Systems, SMART: Bruker Molecular Analysis Research Tool*, Version 5.618; Bruker AXS: Madison, WI2000.
- [2].*Bruker Analytical X-ray Systems, SAINT-NT*, Version 6.04, Bruker AXS: Madison, WI2001.
- [3].*Bruker Analytical X-ray Systems, SHELXTL-NT*, Version 6.10; Bruker AXS: Madison, WI2000.
- [4].Klaus, B. *DIAMOND*, Version 1.2c; University of Bonn: Germany, (1999).