

Supporting Information

Zeolite-Y Encapsulated Cobalt(II) Schiff-Base Complexes Employed for Photocatalytic Dye-Degradation & Upcycling CO₂

Susheela Kumari^a, Aishwarya Ramesh^a, Bidisa Das^b and Saumi Ray^{*a}

^aBirla Institute of Technology and Science, Pilani, Rajasthan 333031.

^bTechnical Research Center (TRC) & School of Applied and Interdisciplinary Sciences (SAIS).

Indian Association for the Cultivation of Science. 2A & 2B Raja S C Mullick Road, Kolkata 700032.

Correspondence

Saumi Ray, Department of Chemistry, Birla Institute of Technology and Science, Pilani, Rajasthan 333031. India.

Email: saumi@pilani.bits-pilani.ac.in

Physical Measurements

The XRD patterns were recorded by a RIGAKU MINIFLEX II X-ray diffractometer using a Cu K α X-ray source ($\lambda = 1.542 \text{ \AA}$) ranging 2θ from 8° to 50° at a scanning rate of 2° min^{-1} . The FESEM-EDX analysis was carried out by using a Zeiss EVO 40 instrument with an accelerated voltage of 5–20 kV and samples were gold-coated before analysis. The N₂ sorption isotherms and Brunauer–Emmett–Teller (BET) surface area and pore volume were recorded on a Quantachrome instruments along with a volumetric adsorption setup at -196°C . Thermogravimetric (TGA) analysis was performed in inert atmosphere within the temperature range of (25–800) $^\circ \text{C}$ by using a TGA-60, SHIMADZU equipment at a heating rate of $10^\circ \text{C min}^{-1}$. The FT-IR measurements were carried out on an ABB FTIR spectrometer with a DRIFT accessory in the range of (450–4000) cm^{-1} by using KBr as a reference. X-ray photoelectron spectroscopic measurement (XPS) was performed on a commercial Omicron EA 125 spectrometer with an Mg K α X-ray

source (1253.6 eV). Samples were used in form of pellets after neutralization and kept in a vacuum oven overnight before XPS. High-resolution XPS traces were deconvoluted by using the Gaussian and Lorentzian statistical analysis in Origin-9 software. The solution UV-vis absorption spectra were recorded by using Shimadzu UV-2100 spectrophotometer. The solid-state UV-vis spectra were performed on a Shimadzu UV-2450 spectrophotometer in reflectance mode by using barium sulfate as a reference. UV-vis spectrophotometer is equipped with an integrating sphere of 60 mm inner diameter and Kubelka–Munk analysis is performed on the reflectance data. The KM factor, $F(R)$, is given by $F(R) = (1 - R)^2 / 2R = k/s$ where R is the diffuse reflectance of the sample as compared to $BaSO_4$, k is the molar absorption coefficient, and s is the scattering coefficient of the sample. Gas chromatographic experiments were performed on a Shimadzu GC-2014 using a FID detector and column RTX-5 with inner diameter of 0.25 mm and film thickness of 0.25 μ m for the catalytic study of neat and encapsulated cobalt(II) Schiff-base complexes.

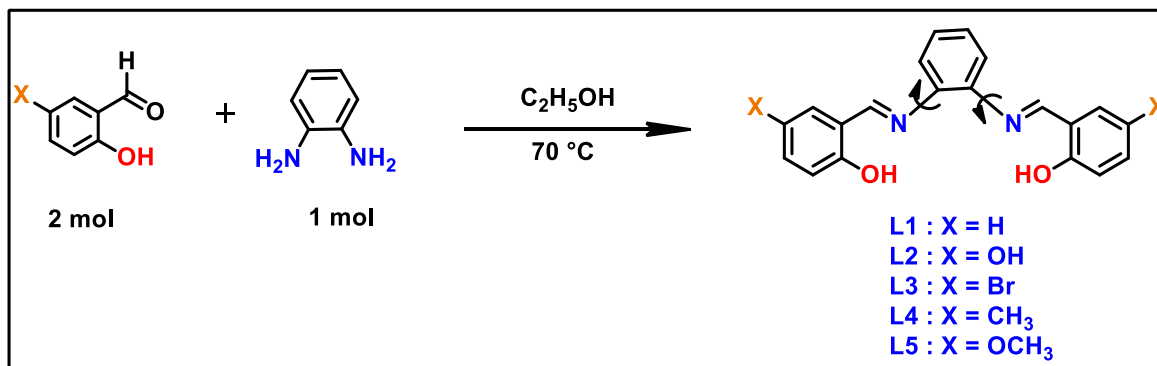
Experimental section

Materials and preparation

The Na-zeolite-Y, 5-hydroxy salicylaldehyde, 5-Bromo- salicylaldehyde, 5-Methyl-salicylaldehyde and 5 - Methoxy-salicylaldehyde are purchased from Sigma-Aldrich, India. Salicylaldehyde is purchased from Merck. Cobalt acetate and all solvents like ethanol, acetone, methanol, ether and acetonitrile are procured from S.D. fine, India.

Synthesis of Schiff base ligands (L1, L2, L3, L4, L5)¹:

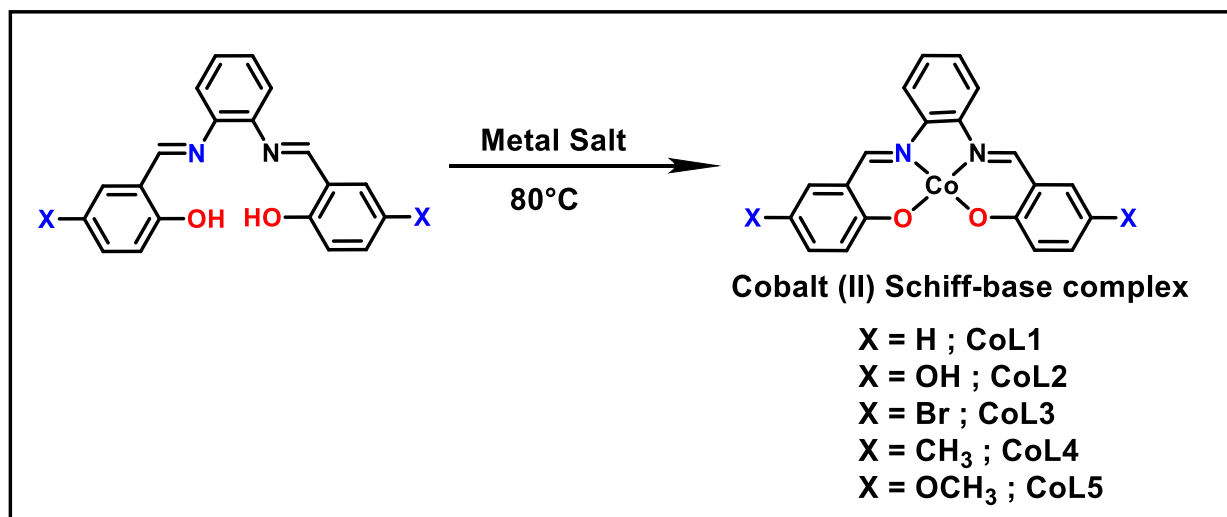
The Schiff base ligands are prepared by the following literature report. 10 mmol of 1,2-phenylenediamine and 20 mmol of salicylaldehyde or its derivatives are refluxed at 70 °C for 4 h in ethanol. At the end of the reaction, the product is filtered out, washed thoroughly with ethanol and finally air-dried (shown in Scheme S1).



Scheme S1: Synthesis of Schiff-base Ligand L1, L2, L3, L4 and L5.

Synthesis of cobalt(II) Schiff-base complexes²:

To synthesize the metal Schiff-base complex, an ethanolic solution of the ligand is heated at 80 °C for 30 minutes and metal salt is added in a 1:1 ligand to metal molar proportion. The reaction mixture is refluxed for 3 h. The solid metal Schiff-base complex is washed with ethanol and finally dried. All the metal complexes are synthesized following same procedure (presented in Scheme S2).



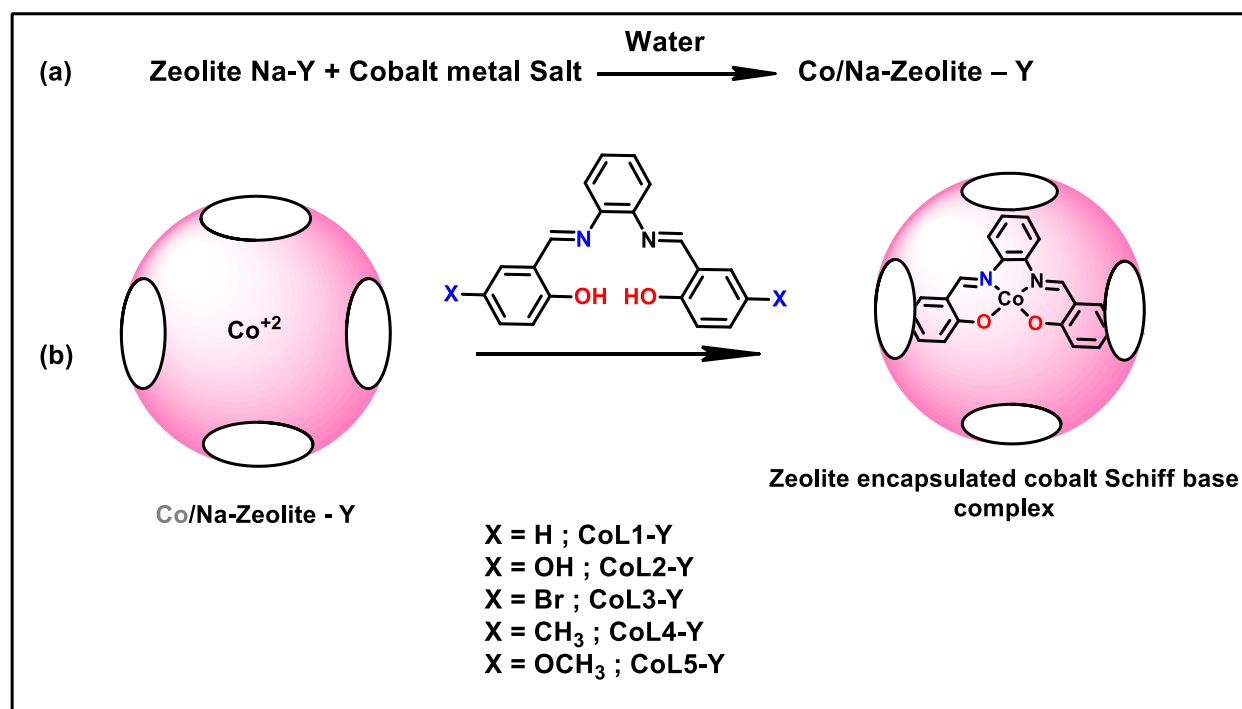
Scheme S2: Synthesis of cobalt(II) Schiff-base Complexes.

Preparation of Cobalt(II)-exchanged zeolite-Y³:

Parent zeolite-NaY (10 g) is allowed to react with 0.01 M metal salt $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}] = 0.177\text{ g}$ in 100 mL of distilled water to acquire the required loading level of metal ions and stirred at room temperature for 24 h. The slurry is filtered, washed repeatedly with water, and then desiccated for 12 h at 150 °C (presented in Scheme S3).

Preparation of encapsulated Cobalt(II)–Schiff base complexes in zeolite-Y^{4,5}:

The Cobalt(II)-exchanged zeolite-Y is treated with a stoichiometric excess of respective Schiff-base ligand. Being a flexible ligand, it diffuses through the channels of the host when the reaction mixture is refluxed for 24 h at 150-200 °C under constant stirring and reacts with the metal ions present in the supercage. The color of solid reaction mass changes from yellowish to dark brown. The reaction mass is then recovered and dried at room temperature. The resultant product is further purified by Soxhlet extraction maintaining the sequence of solvents as acetone, methanol, and finally with diethyl ether to remove unreacted ligand and metal complex adsorbed on the surface of the host. The obtained product is then dried in muffle furnace at 150 °C for 12 h. The product is allowed to react with 0.01M NaCl solution to remove the unreacted metal ions, finally followed by filtration and washed with distilled water thoroughly until the filtrate is negative for chloride ion test. Finally, zeolite encapsulated metal Schiff base complexes are obtained as dark brown powders (given in Scheme S3).



Scheme S3: (a) Synthesis of cobalt(II)-exchanged zeolite-Y and (b) synthesis of zeolite encapsulated cobalt(II) Schiff-base complexes via flexible ligand synthesis method.

Catalytic reactions

Degradation of rhodamine B:

0.1197 g of Rhodamine-B dye is added to a 250 mL milli-Q deionized water in a volumetric flask, to prepare a 1 mmol stock solution of Rhodamine B dye. For catalytic reaction, 1 mL of stock solution was further added to a 50 mL volumetric flask having milli-Q water, to get a 20 μ M solution of Rh-B dye. This solution of Rhodamine-B dye (50 mL) taken in a beaker, free-state or encapsulated Cobalt(II) Schiff base complex is added as catalyst and H_2O_2 is used as oxidant. Reaction mixture is kept on a magnetic stirrer and irradiated in presence of UV light (12 Watts, 254 nm). A series of runs are performed to figure out the optimum amount of metal complex catalyst and the oxidant. 0.0036 mmol of metal complex and 0.88 mmol of H_2O_2 are finalised as optimum amounts of catalyst and oxidant respectively. The degradation of dye has been monitored by using UV-Vis spectrophotometer at different time intervals within the range of 200-800 nm. The aliquot samples of the reaction mixture is collected at certain time intervals and spectral changes are analyzed at the wavelength of 554 nm (λ_{max} of rhodamine B dye). The percentage of the degradation has been calculated by using Lambert-Beers law. ($A = \epsilon \cdot c \cdot l$; where A = Absorbance, ϵ = molar extinction coefficient [$\text{M}^{-1} \text{cm}^{-1}$], c = concentration of sample, l = path length in cm).

Cycloaddition of CO_2 to styrene oxide:

10 mmol (1.13ml) of styrene oxide, 25mg of the encapsulated complex (CoL1-Y or CoL5-Y) and 0.05 mmol (16.1 mg) of tetrabutylammonium bromide (TBAB) were taken in a teflon container. The teflon container was put in the stainless-steel chamber of the pressure reactor and was sealed. This reaction mixture was supplied with a continuous flow of CO_2 . The temperature was set to 130° C, and the reaction was carried out for 1.5h. After the specified time, the excess CO_2 was released, and the reactor was opened after it cooled down to room temperature. The reaction mixture was diluted with 10 ml of acetonitrile and transferred in a glass vial. From this vial, 1.5 ml of the reaction mixture was taken in 2 ml eppendorf tube, and 0.45 ml of internal standard, i.e., Bromobenzene (PhBr), was added. This mixture was centrifuged and was used for gas chromatography.

The same process was followed for catalysis with the neat complex. The amount of complex and TBAB taken were 0.025 mmol

Figure S1:

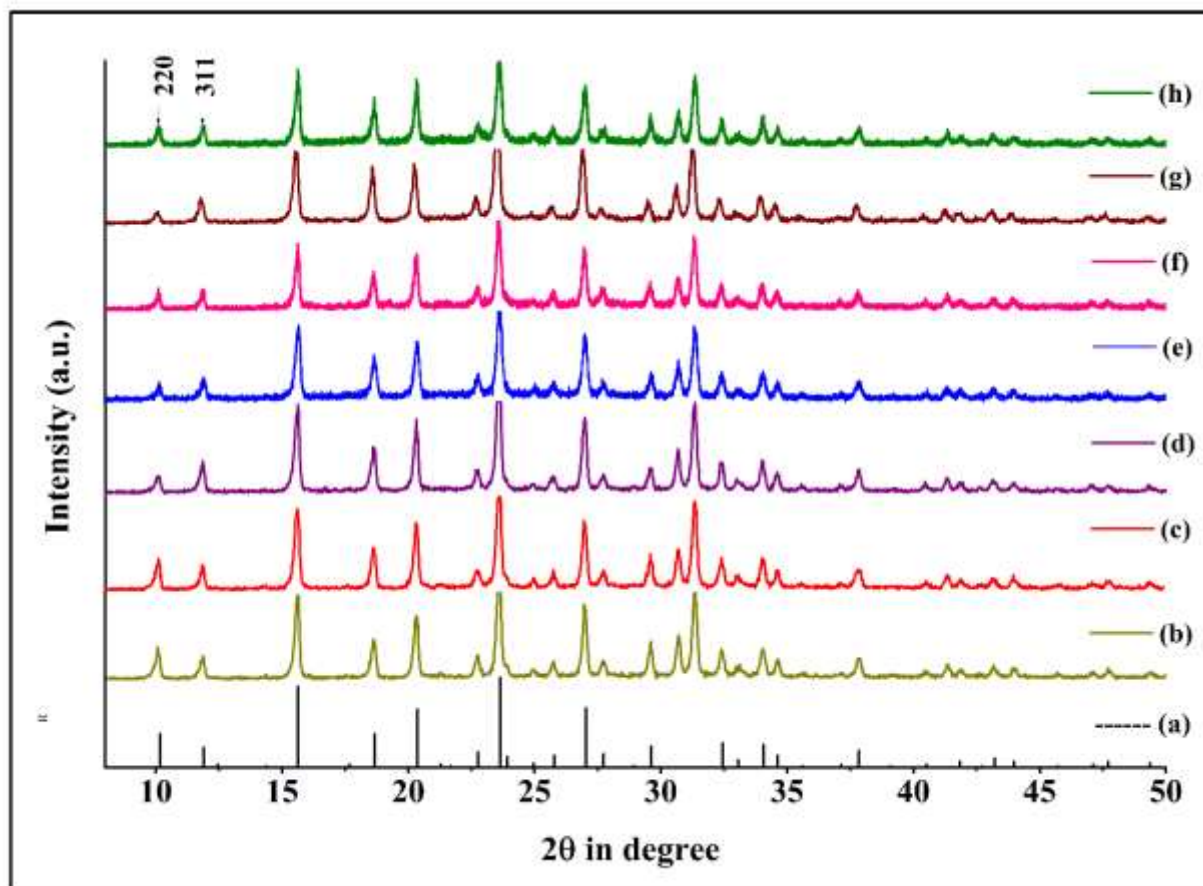


Figure S1: Powder XRD patterns of (a) JCPDS reference pattern of zeolite-Y (JCPDS No. 043-0168) (b) pure zeolite-Y (c) Cobalt(II)-exchanged zeolite-Y (d) CoL1-Y, (e) CoL2-Y, (f) CoL3-Y, (g) CoL4-Y and (h) CoL5-Y.

We can clearly see that the peaks of pure zeolite-Y are in well agreement with its JCPDS data except the peak at 2θ value around 32° , which is absent in the JCPDS data. However, several reports in literature indicate the presence of quite a prominent peak at 32° in the XRD pattern of zeolite-Y which is exactly in line with our observation.⁶⁻⁸

Figure S2:

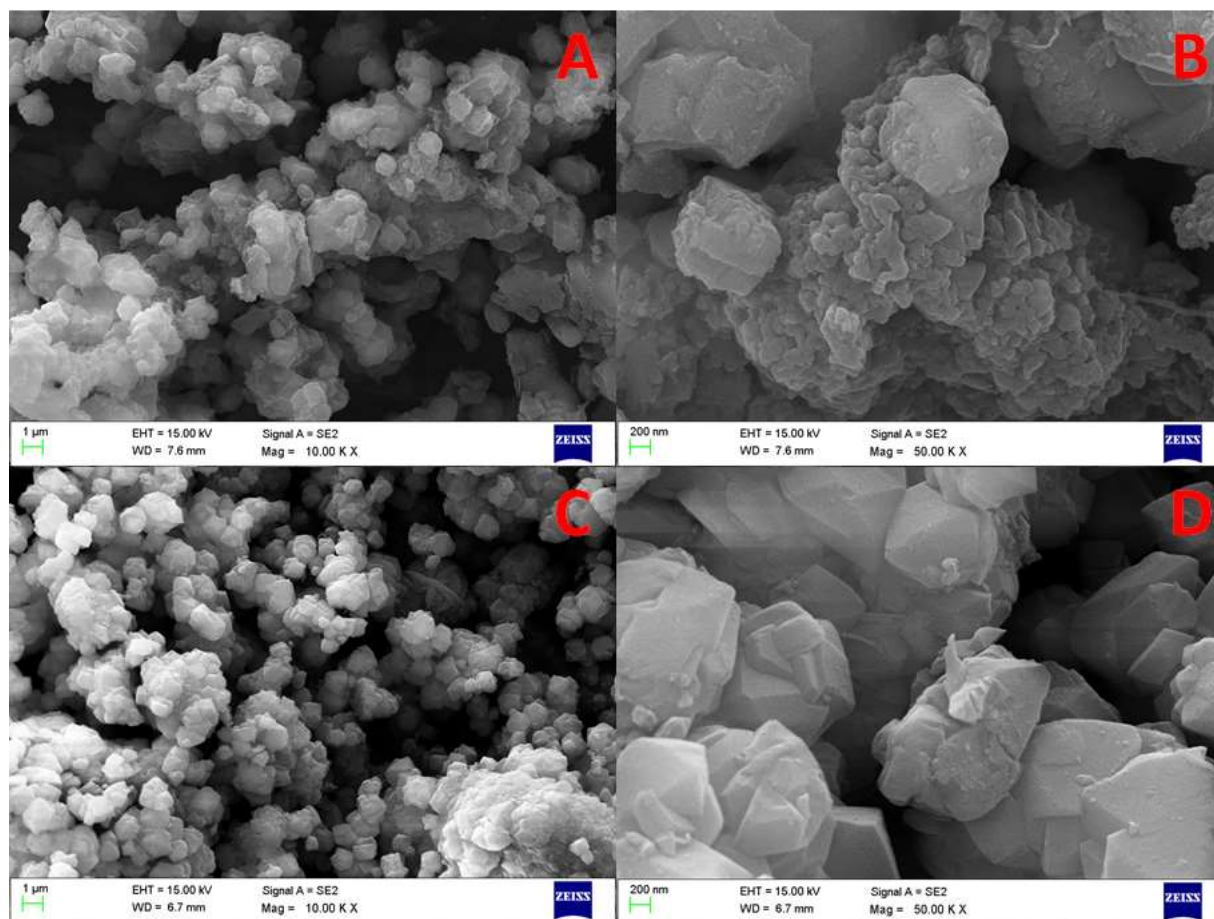


Figure S2: SEM images before Soxhlet extraction (A-B) CoL5-Y with different resolution, and after Soxhlet extraction (C-D) CoL5-Y.

Figure S3:

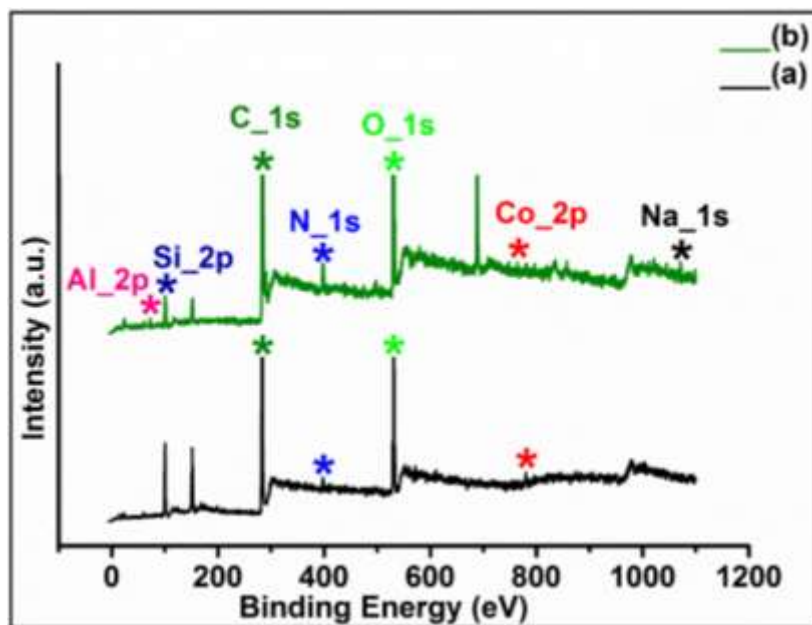


Figure S3: XPS survey spectra of (a) CoL5 and (b) CoL5-Y.

Figure S4:

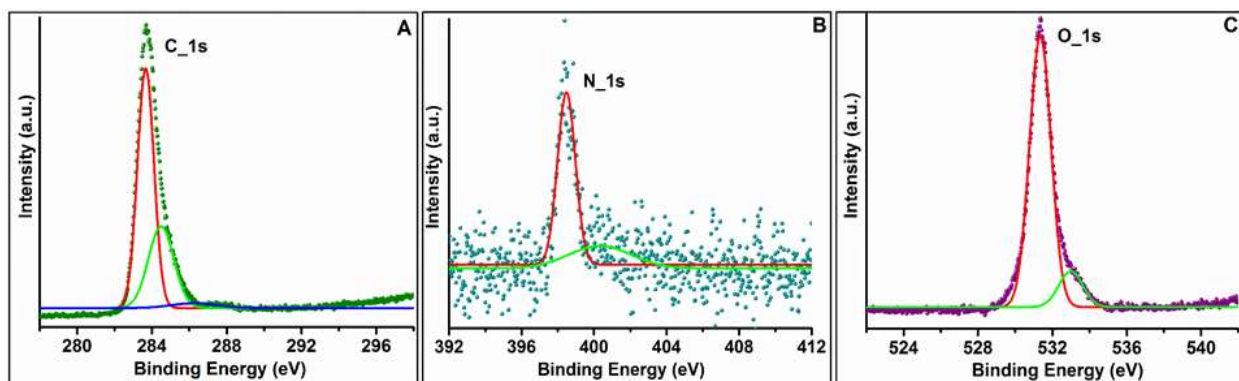


Figure S4: High-resolution peak fitted XPS spectra of (A) C (1s), (B) N (1s) and (C) O (1s) for CoL5.

Figure S5:

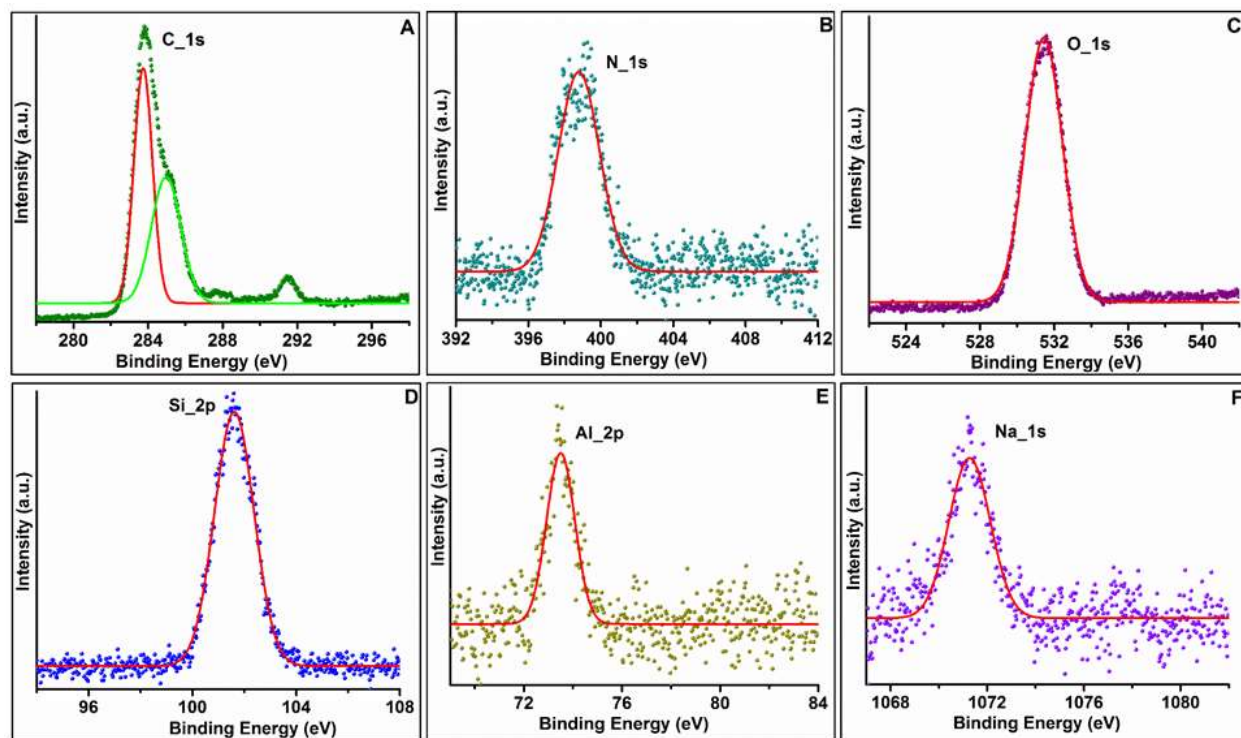


Figure S5: High-resolution XPS spectra of (A) C (1s) (B) N (1s) (C) O (1s) (D) Si (2p) (E) Al (2p) and (F) Na (1s) for CoL5-Y.

FTIR Spectroscopic Study

The FTIR spectral data of pure zeolite-Y and encapsulated Cobalt(II) Schiff base complexes are presented in Figure S6. It is clear from the FTIR spectra that the characteristics IR bands of zeolite-Y dominate the spectra below 1200 cm^{-1} . FTIR spectra of pure zeolite-Y (Figure S6) show strong IR peaks in the range $500\text{--}1200\text{ cm}^{-1}$. The strong IR peak at the region $1010\text{--}1040\text{ cm}^{-1}$ attributed due to the asymmetric stretching vibrations of (Si/Al) O_4 units of zeolite framework. The prominent broad bands appeared at 1643 and 3500 cm^{-1} are assigned due to lattice water molecules and surface hydroxylic groups, respectively. Some other characteristics bands at 560 , 717 , and 786 cm^{-1} (Figure S6) are attributed to T–O bending mode, double ring and symmetric stretching vibrations respectively. These IR bands are not modified during the encapsulation process (Figure S6). The characteristic FTIR bands of zeolite framework remain unaltered during metal exchange reaction and encapsulation process implies that the zeolite framework maintains its

integrity upon encapsulation of cobalt(II) Schiff-base complexes. However, there is noticeably a difference in the spectral range of 1200–1600 cm^{-1} for the encapsulated complex (see Figure S6). This region is suitable region for the study of encapsulated complexes because the zeolite framework does not show any absorption band and FTIR bands observed are only because of the complexes that lie in the range of 1200–1600 cm^{-1} . The IR peaks of encapsulated cobalt(II) Schiff base complex are very weak due to their low loading level in the zeolite supercage. The important FTIR bands are assigned in Table S1 for both the neat and encapsulated cobalt complexes.

Two strong FTIR bands of the ligands observed at 1612-1620 cm^{-1} and 1273-1296 cm^{-1} are correspond to the C=N and C-O stretching vibrations and these bands are slightly shifted towards lower frequency upon complexation, indicating nitrogen and oxygen coordination inside the cavity of zeolite-Y. IR spectra of neat cobalt complex exhibit two strong bands at 1593-1609 cm^{-1} and 1257-1296 cm^{-1} are characteristic of C=N and C-O stretching vibrations. The bands at 1444- 1539 cm^{-1} are assigned to C=C stretching and peak at 1373-1396 cm^{-1} is attributed to $\nu_{\text{C-H}}$ deformation. In the FTIR spectra of encapsulated system, all IR bands are very less intense. This characteristic further reveals the nonexistence of extraneous metal complex on the external surface of zeolite-Y. The presence of similar FTIR vibrational bands in the neat and encapsulated complexes gives indirect evidence for the presence of a cobalt(II) Schiff-base complex inside the super cage of zeolite-Y. The slight shifting in the IR peak positions can be attributed due to the effect of zeolite framework on the geometry of the cobalt complexes trapped in the zeolite cavities. The shift in $\nu_{\text{C-H}}$ deformation frequency after encapsulation of metal complex provides the evidence for the encapsulation of metal complex inside the cavity of zeolite-Y.

Figure S6:

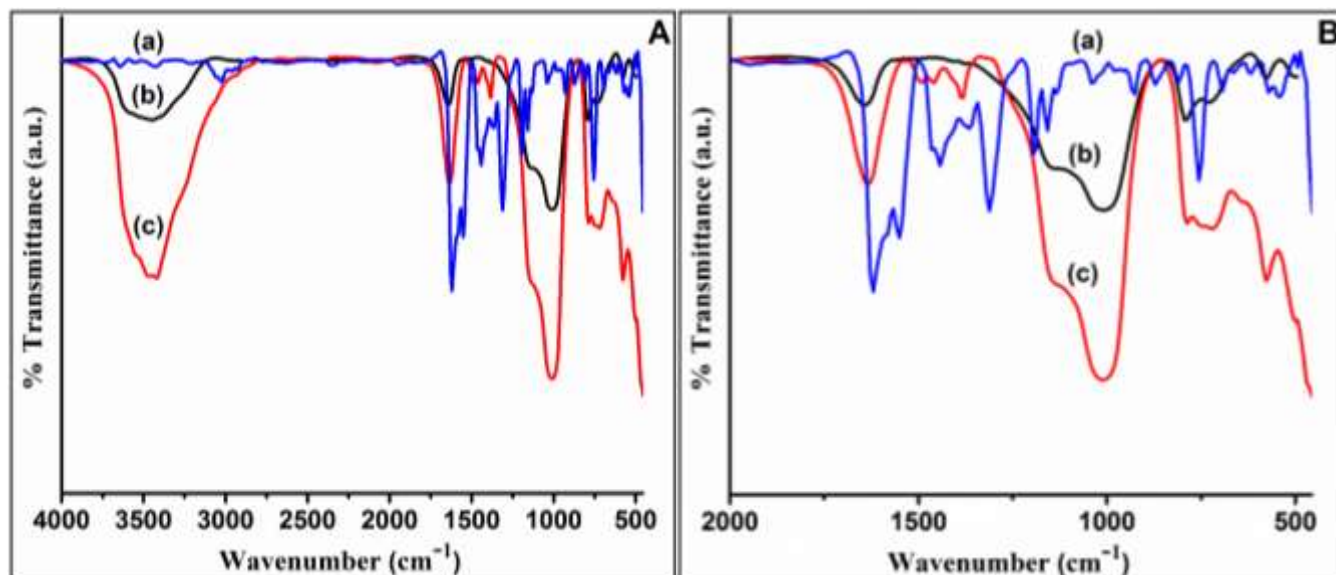


Figure S6: (A) FTIR spectra of (a) free-state cobalt salophen complex CoL1, (b) pure zeolite-Y and (c) encapsulated cobalt salophen complex CoL1-Y. (B) Enlarged view of FTIR spectra of (a) free-state CoL1 complex, (b) pure zeolite-Y and (c) encapsulated complex CoL1-Y.

Table S1: FTIR data of free-state and zeolite encapsulated complexes.

S. No	Samples	C=N stretching	C=C stretching	C-H deformation	C-O stretching
1	CoL1	1622	1548, 1464	1368	1307
2	CoL1-Y	1631	1492, 1458	1386	1276

Thermal analysis

To know the thermal stability of free-state and encapsulated cobalt complexes thermo-gravimetric analysis (TGA) has been performed. TGA experiment is carried out in the temperature range of (25-800) °C under nitrogen atmosphere along with 10 °C/minute heating rate. The TGA results for free-state and encapsulated

cobalt system are shown in Figure S7. The TGA analysis of zeolite entrapped cobalt complex stipulate two steps. First step occurs in the temperature range of (30 – 180) °C and is attributed to the loss of intrazeolite water molecules.⁹ Second step arises in a broad temperature range of (300–750) °C indicating slow decomposition of chelating ligand. A very small weight loss actually suggests quite a low loading level of entrapped cobalt complex within the supercage of zeolite framework and these results are well-consistent with the weight% of cobalt metal estimated by the EDX analysis. Encapsulated cobalt complexes show that the weight loss temperature extends towards higher temperature, which indicates that the zeolite encaged cobalt complex is more thermally stabile as compared to the neat complexes.

Figure S7:

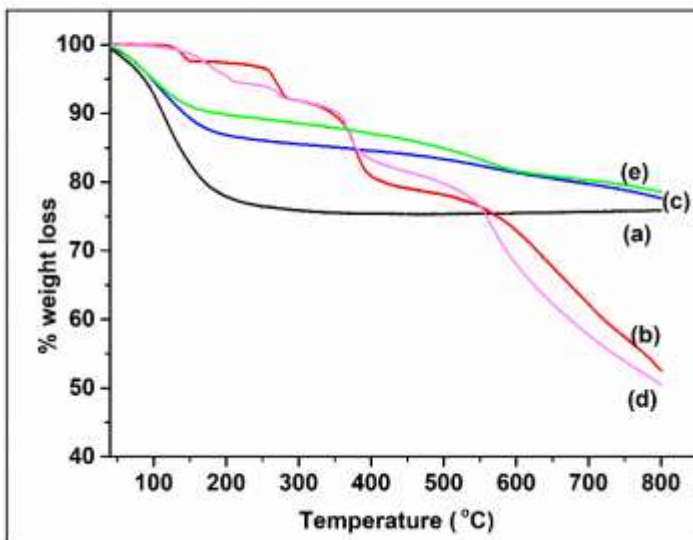


Figure S7: TGA curves of (a) Pure zeolite-Y (b) CoL1 (c) CoL1-Y (d) CoL5 and (e) CoL5-Y.

Solution UV studies:

Figure S8

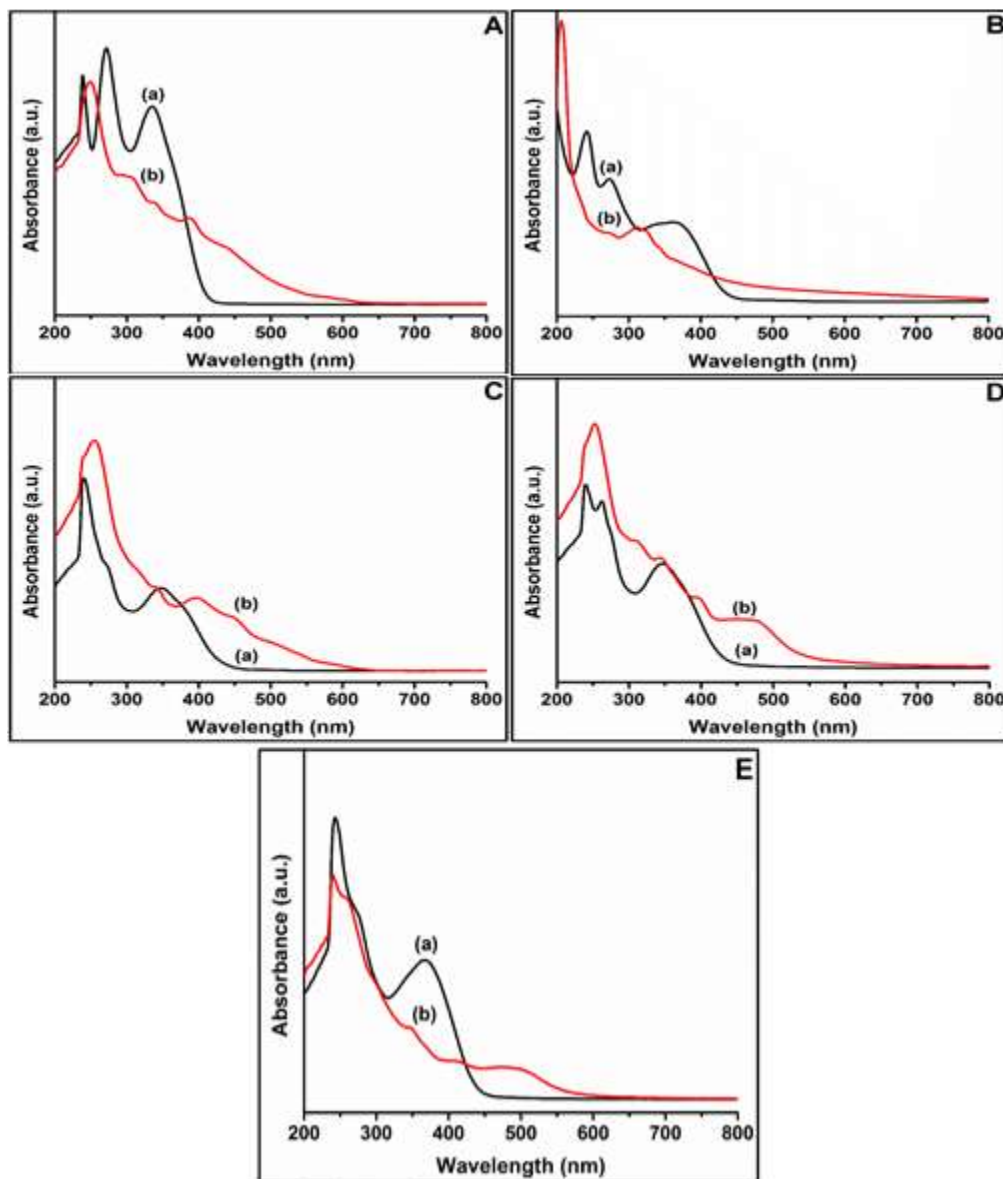


Figure S8: The solution UV-Vis spectra of Schiff base ligands and cobalt(II) Schiff base complexes (A) (a) L1 and (b) CoL1 (B) (a) L2 and (b) CoL2 (C) (a) L3 and (b) CoL3 (D) (a) L4 and (b) CoL4 (E) (a) L5 and (b) CoL5.

Table S2: Solution UV-Vis data of ligand and neat complexes

S. No	Samples	$\pi\text{--}\pi^*$ transitions	$n\text{--}\pi^*$ transitions	CT transitions / d-d transitions
1	L1	272, 283	335, 364	-
2	CoL1	248, 302	340, 388	440, 583
3	L2	241, 273	354, 370	-
4	CoL2	235, 271	315, 376	490, 596
5	L3	240, 271	349, 382	-
6	CoL3	255, 315	342, 396	502, 594
7	L4	239, 263	347, 385	
8	CoL4	238, 252	344, 396	478, 586
9	L5	244, 279	302, 375	
10	CoL5	239, 260	305, 350	500, 580

Theoretical Methods

The theoretical studies presented in the manuscript are based on Density Functional Theory (DFT), which we have employed to study and analyse the structural and optical properties of the CoL1, CoL2 and CoL5 complexes in neat and zeolite encapsulated states. All results presented here are calculated using GAUSSIAN 09 suite of *ab initio* quantum chemistry programs.¹⁰ All the structural optimizations were done using hybrid B3PW91¹¹⁻¹⁴ exchange and correlation functional with double-zeta 6-31G** basis-set for all atoms. Vibrational frequencies were calculated for all complexes and it was ascertained that all the structures were stable when no symmetry constraints are imposed.

In the studies involving encapsulation of Cobalt complexes within zeolite pore, we have modelled only a portion Zeolite-Y supercage as shown in Figure 5.1d in the main manuscript, and all the unsatisfied valancies of Silicon atoms are terminated by Hydrogen atoms. During the study of encapsulated complexes, the structure of the zeolite supercage was kept fixed without any relaxations, however the positions of the terminal hydrogen atoms were allowed to change. This approach had been used for several other studies, where zeolite encapsulated transition metal based Schiff-base complexes were studied.¹⁵⁻¹⁸ Cobalt(II) being

a d^7 system, we have studied the doublet, neat and quartet, encapsulated states of the Cobalt-complexes, and the optical spectra are calculated using time dependent density functional (TD-DFT) methods. For these studies we used B3PW91/6-31++G** for all atoms on B3PW91/6-31G** optimized structures. In case of quartet encapsulated complexes, the optical spectra are calculated without the zeolite supercage, *i.e.* after extracting the encapsulated Cobalt-complexes from zeolite and keeping its geometry fixed. The optical spectra is then analysed in terms of the molecular orbitals of the Cobalt-complexes in free or encapsulated states, thus the plots for frontier molecular orbitals of the complexes are shown here. The molecular orbitals are defined with respect to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as HOMO-n (H-n) and LUMO+n (L+n). Since the Cobalt(II) d^7 complexes are commonly known to dimerize, we also looked into dimerization of the Cobalt-complexes studied. The binding energy for the dimer formation is calculated as:

$$E_{\text{bind}} = 2(E_{\text{monomeric Co-complex}}) - E_{\text{dimeric Co-complex}}$$

We performed structural studies for CoL1, CoL2 and CoL5, of which CoL1 and CoL5 are given in the main manuscript. Below we present the optimized structure of CoL2 and CoL5 in Figure S9 and structural details for CoL2 in Table S2. We also show the optimized structures of singlet and triplet states of dimer of CoL1 in Figure S10 and structural details are given in Table S3. Frontier molecular orbitals of doublet states of CoL1, CoL2 and CoL5, ground triplet states of dimers of CoL1, CoL2 and CoL5, and excited, quartet states of CoL1, CoL2 and CoL5 are all shown below in Figures S11-19. We report the TD-DFT spectra of CoL1, CoL2 and CoL3 in doublet states in Figure S20. The TD-DFT spectra for dimer of CoL2 and CoL5 in triplet state is given in Figures S21 and S22, while the spectra for quartet, excited states of CoL2 and CoL5 are shown in Figures S23 & S24.

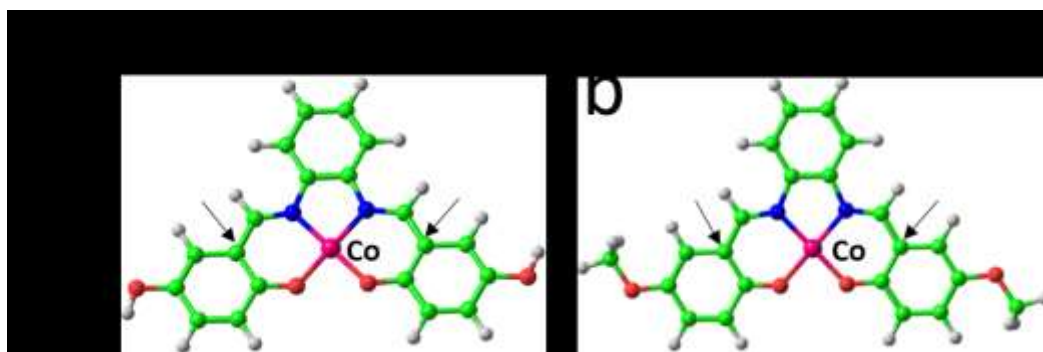


Figure S9. The optimized structure of CoL2 (a) and CoL5 (b) in doublet states. The C-atom marked by black arrow has been used to define the bond-angles in Table 5.

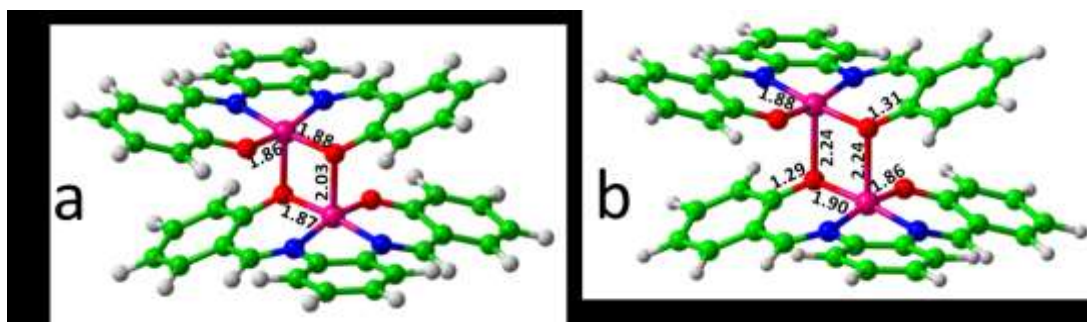


Figure S10. The dimer of CoL1 in singlet (a) and triplet state (b), with few bond-distances marked.

Table S3. Selected structural parameters and molecular orbital energies for CoL2. The doublet, neat and encapsulated, quartet states have been listed. Alpha and beta orbitals are marked by (a) and (b).

S. No	Bond distances / angles	CoL2	CoL2-Y
		Doublet	Quartet
1	Co-O (Å)	1.82	1.90
2	Co-N (Å)	1.86	2.01
3	O-C (Å)	1.29	1.29
4	N-C (Å)	1.32	1.31
5	<O-Co-N(°)	94.4	91.2
	<C-Co-C(°)	178.7	175.1
6	<Co-N-N-O(°)	-0.1	-12.0

	<N-N-O-O(°)	0.2	22.9
7	End to end distance (Å)	14.3	14.4
8		-5.11 (a)	-4.98(a)
	HOMO (eV)	-5.13 (b)	-5.14(b)
9		-2.18 (a)	-2.20(a)
	LUMO (eV)	-2.23 (b)	-2.24(b)
10	HOMO-LUMO gap (eV)	2.88	2.74
11	Spin density on Co	1.04	2.77

Table S4. Selected structural parameters and molecular orbital energies for the dimer of CoL1, CoL2 and CoL5. Both the singlet and triplet states are listed. The molecular orbitals are marked (a) and (b) for alpha and beta spins, respectively.

S. No	Bond distances / angles	dimer-CoL1 Singlet	dimer - CoL2 Singlet	dimer – CoL5 Singlet	dimer - CoL1 Triplet	dimer - CoL2 Triplet	dimer – CoL5 Triplet
1	Co-O (Å)	2.03	2.02	2.03	2.24	2.24	2.24
	Vertical Co-O (Å)	1.86,188	1.86,1.89	1.86,189	1.86,1.90	1.86,1.90	1.86,1.90
	lateral						
2	Co-N (Å)	1.88	1.88	1.88	1.88	1.88	1.88
3		1.29	1.29	1.29	1.29	1.29	1.29
	O-C (Å)	1.32	1.33	1.33	1.31	1.31	1.31
4	N-C (Å)	1.31	1.31	1.31	1.31	1.31	1.31
5	<O-Co-N (°)	93.2,94.2	93.1,94.2	93.2,94.2	92.8, 94.5 152.5	92.9, 94.4 153.1	92.6, 94.5
	<C-Co-C (°)	151.3	152.9	152.8			153.1
6							
	<Co-N-N-O(°)	-4.2, -10.9	-3.8, -11.5 -8.4, -8.0	-4.9, -11.5 -8.1, -8.0	-2.7, -8.7	-3.0, -9.0	-2.6, -8.8
	<N-N-O-O (°)	-7.2, -10.9			6.3	6.5	6.5

7	End to end distance, diagonal(Å)	14.9	15.4	19.0	15.0	15.6	19.2
8	HOMO (eV)	-3.79	-3.71	-3.65	-4.95 (a) -4.75 (b)	-4.66 (a) -4.55 (b)	-4.59 (a) -4.48 (b)
9	LUMO (eV)	-2.15	-2.06	-2.00	-1.95 (a) -1.97 (b)	-1.97 (a) -1.98 (b)	-1.90 (a) -1.92 (b)
10	HOMO-LUMO gap (eV)	1.64	1.65	1.65	2.78	2.57	2.56
11	Spin density on each Co	None	none	none	1.07,1.07	1.08,1.08	1.08,1.08

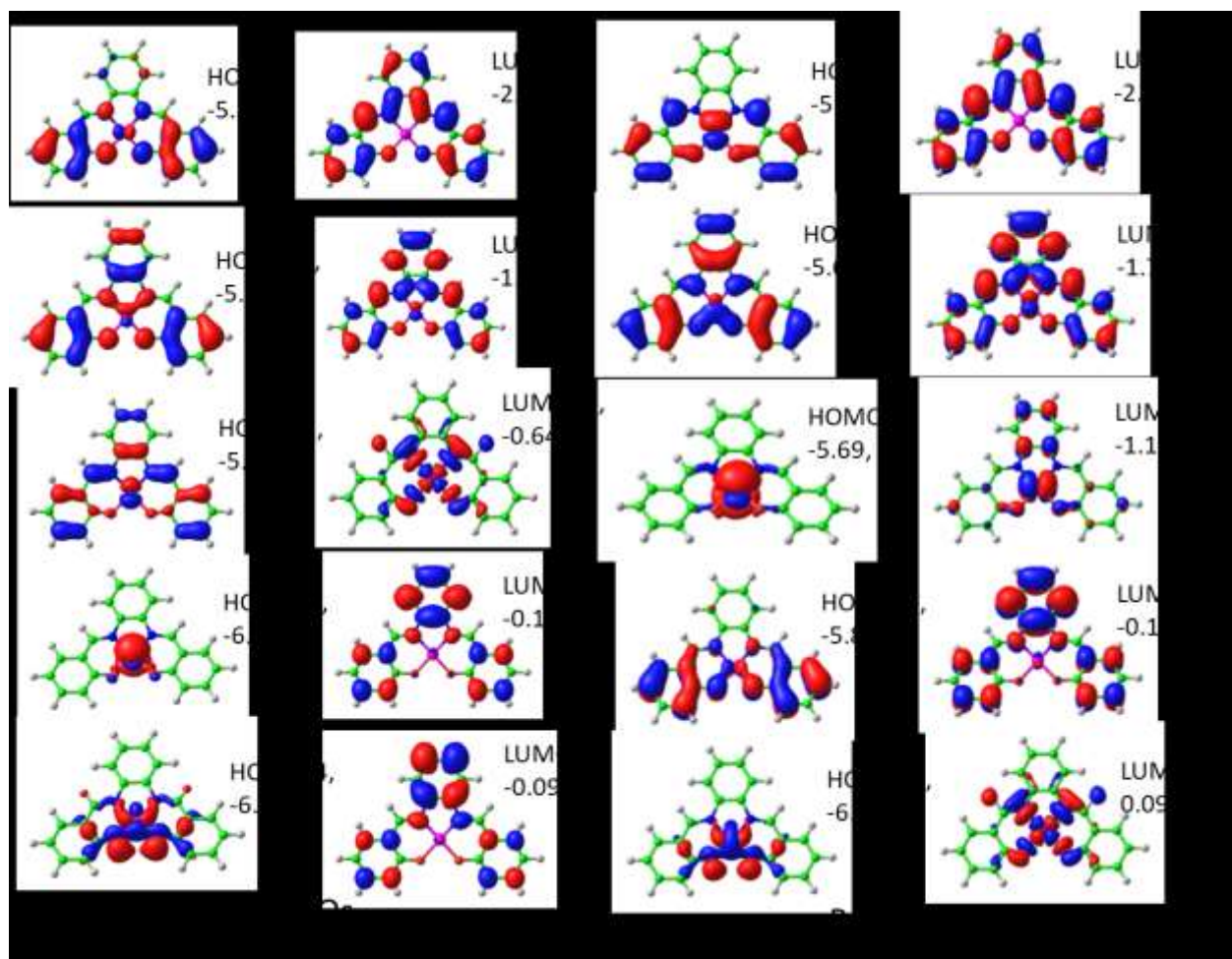


Figure S11: The molecular orbitals of CoL1 monomer in doublet spin state. The energies are in eV.

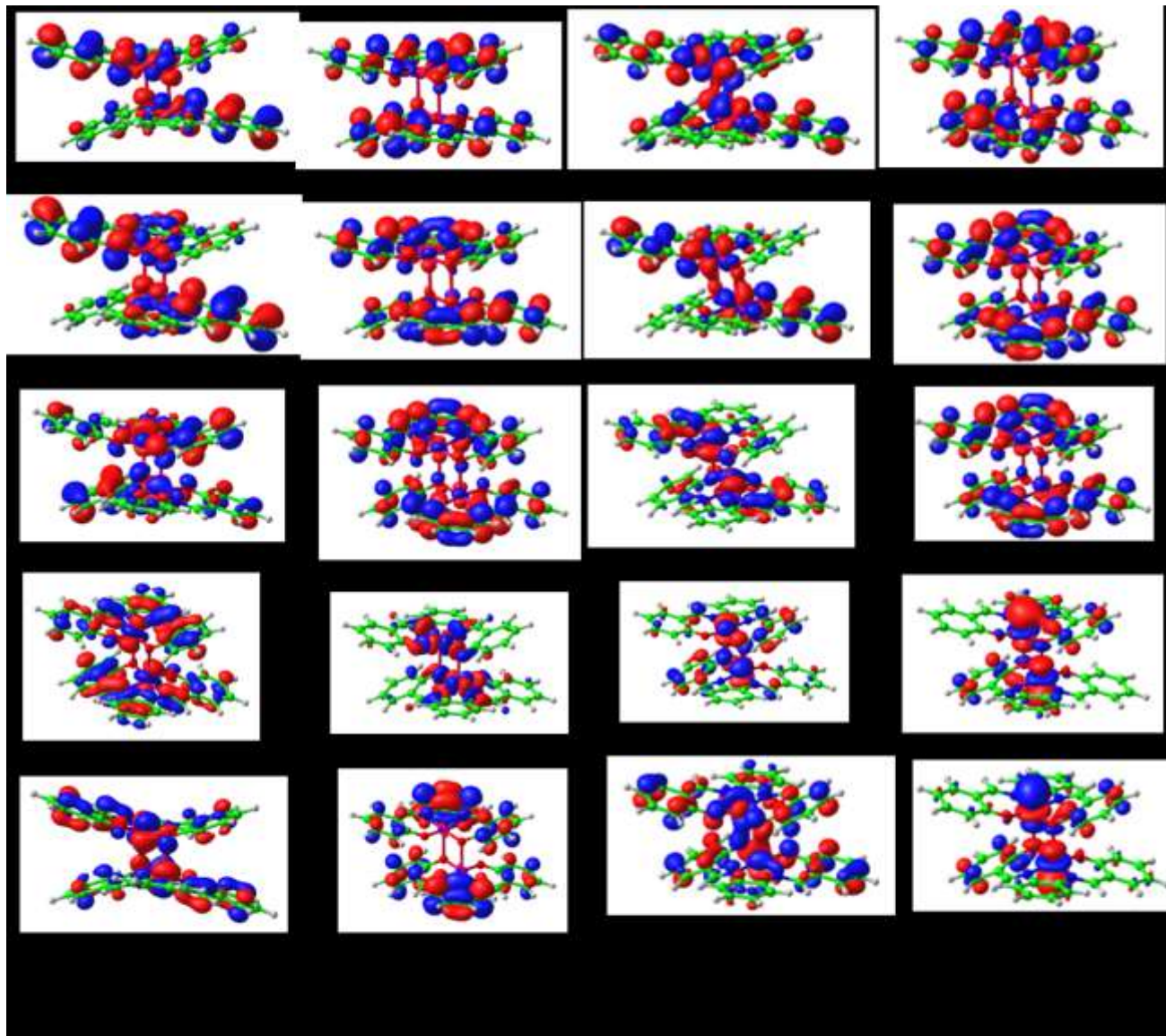


Figure S12: The molecular orbitals of CoL1 dimer in triplet spin state. The energies are in eV.

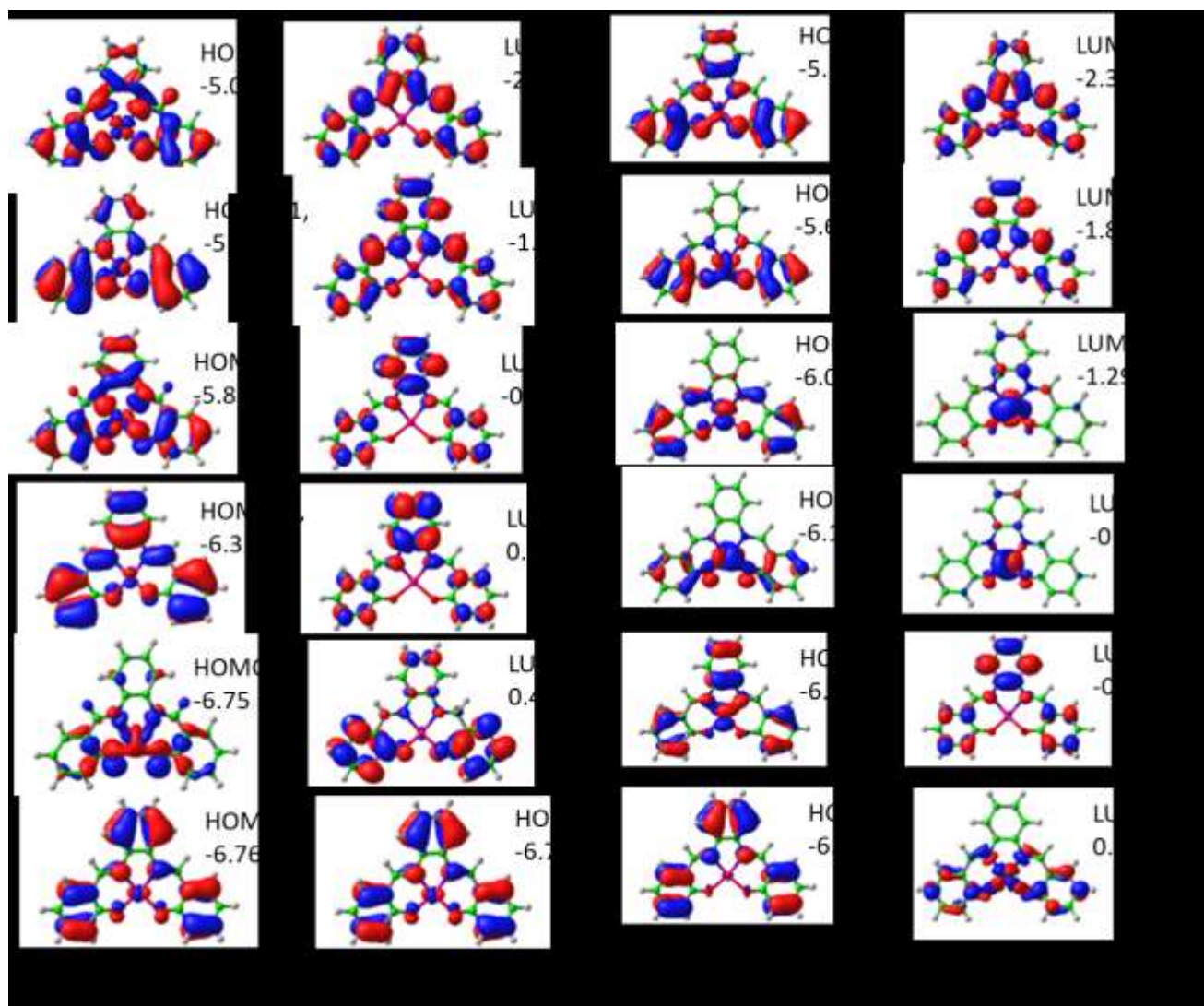


Figure S13: The molecular orbitals of CoL1, encapsulated and extracted in quartet spin state. The energies are in eV.

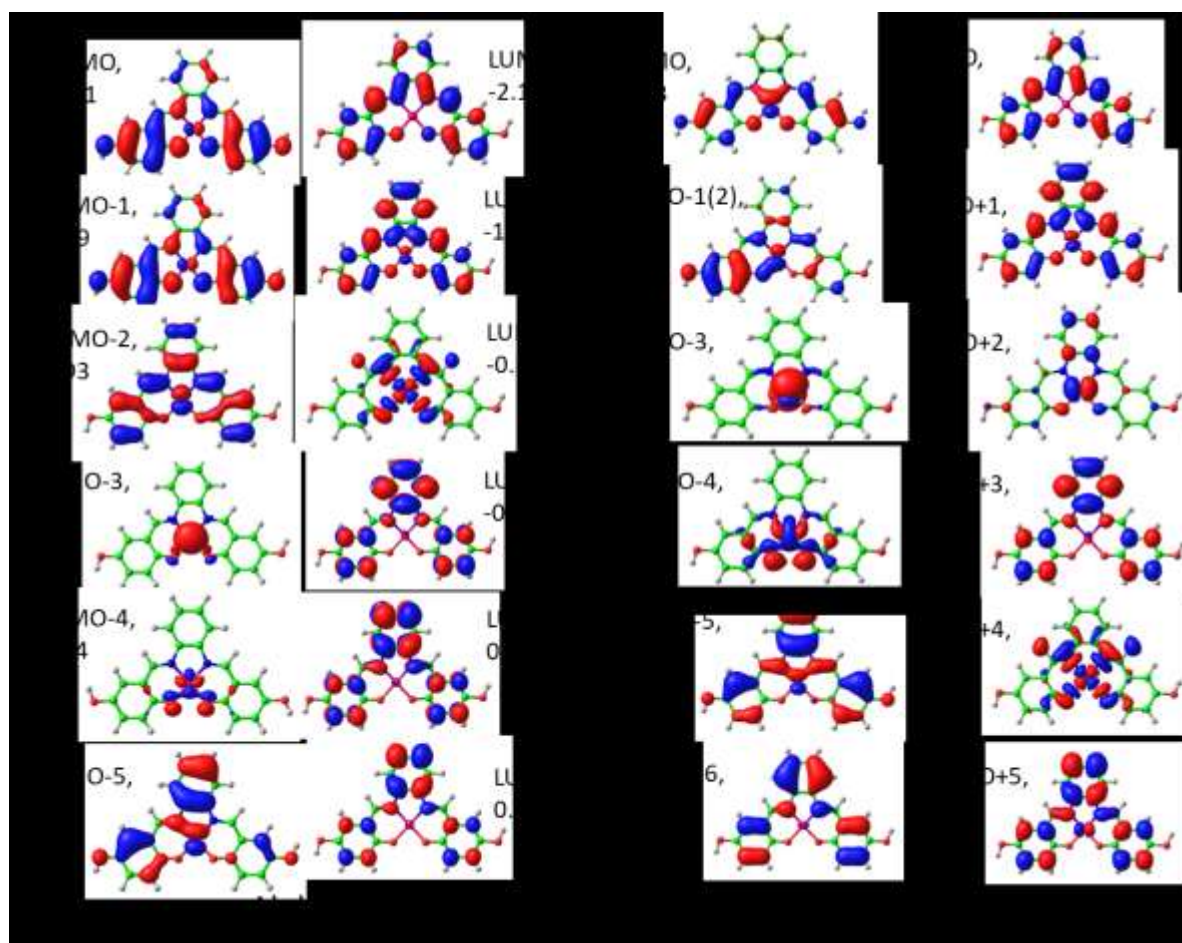


Figure S14: The molecular orbitals of CoL2 monomer in doublet spin state. The energies are in eV.

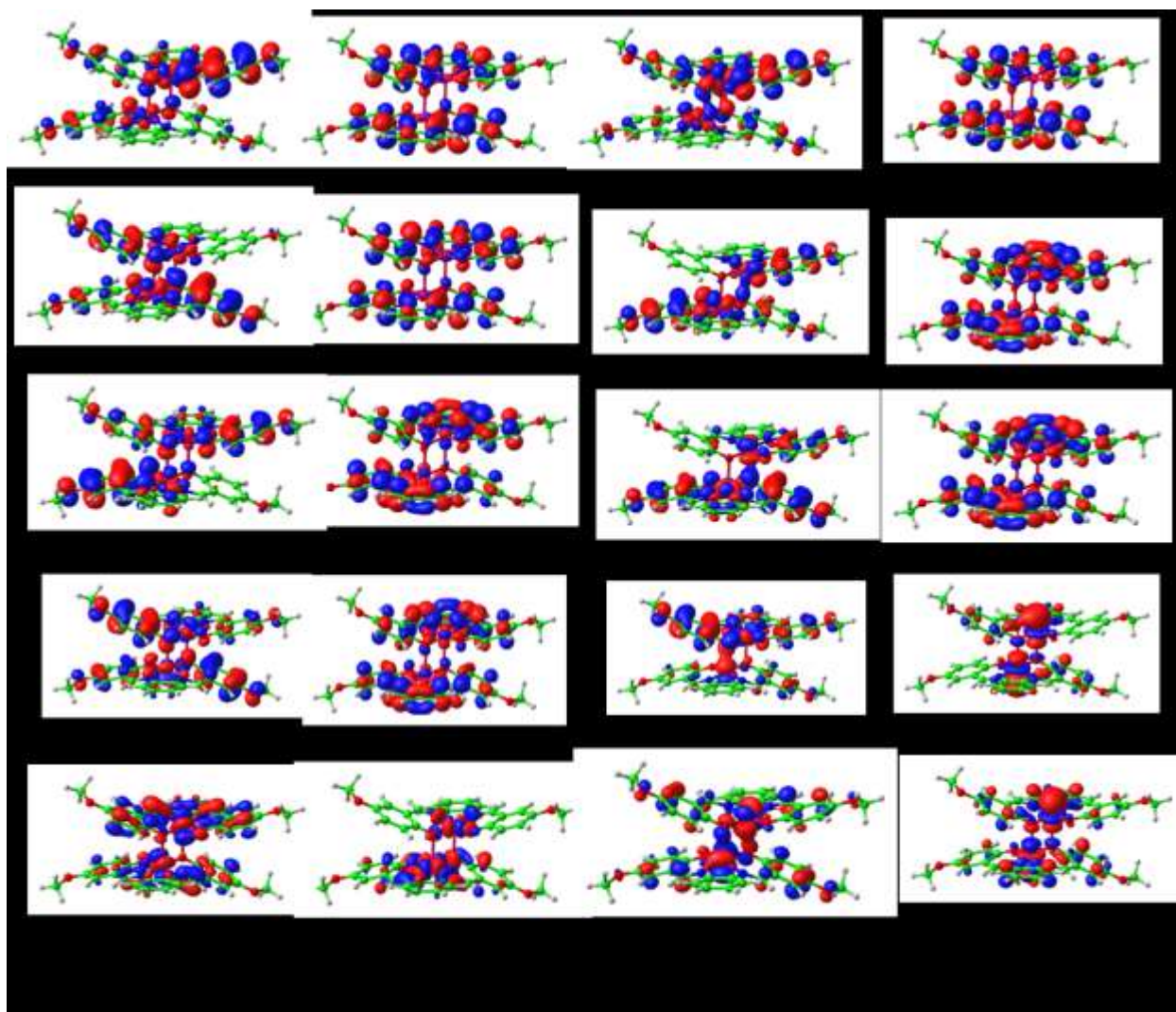


Figure S15: The molecular orbitals of CoL2 dimer in triplet spin state. The energies are in eV.

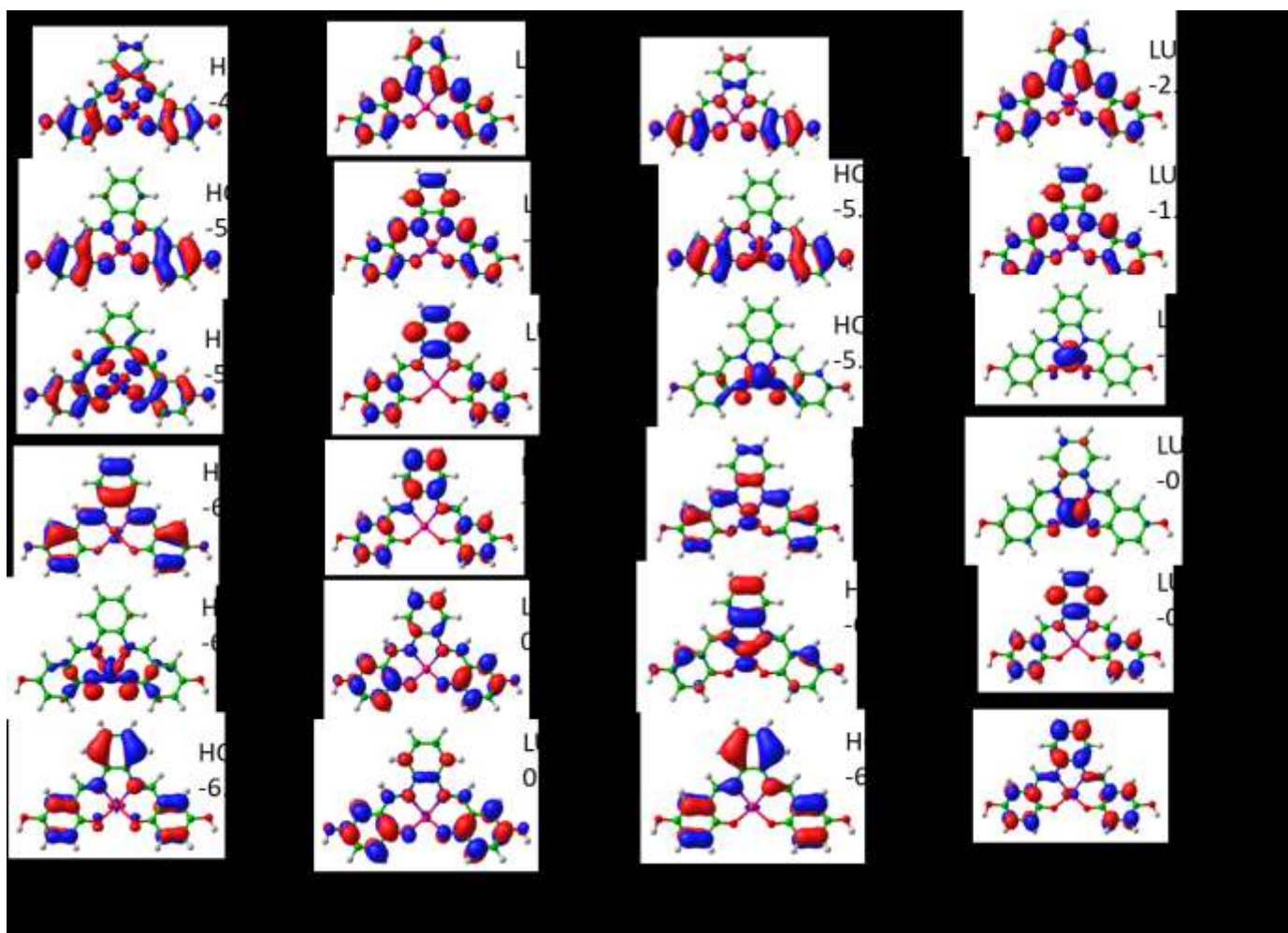


Figure S16: The molecular orbitals of CoL2, encapsulated and extracted in quartet spin state. The energies are in eV.

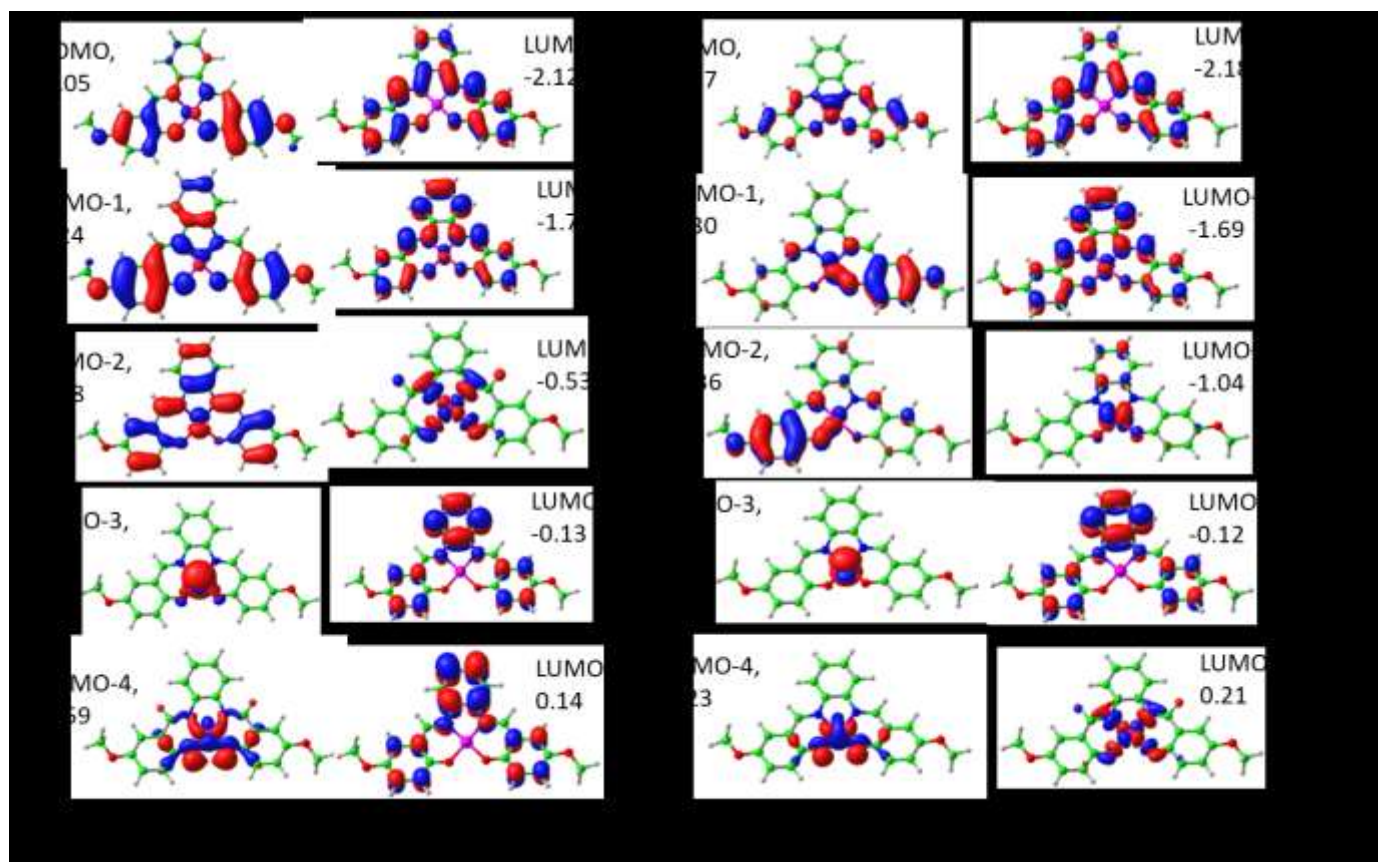


Figure S17: The molecular orbitals of CoL5 monomer in doublet spin state. The energies are in eV.

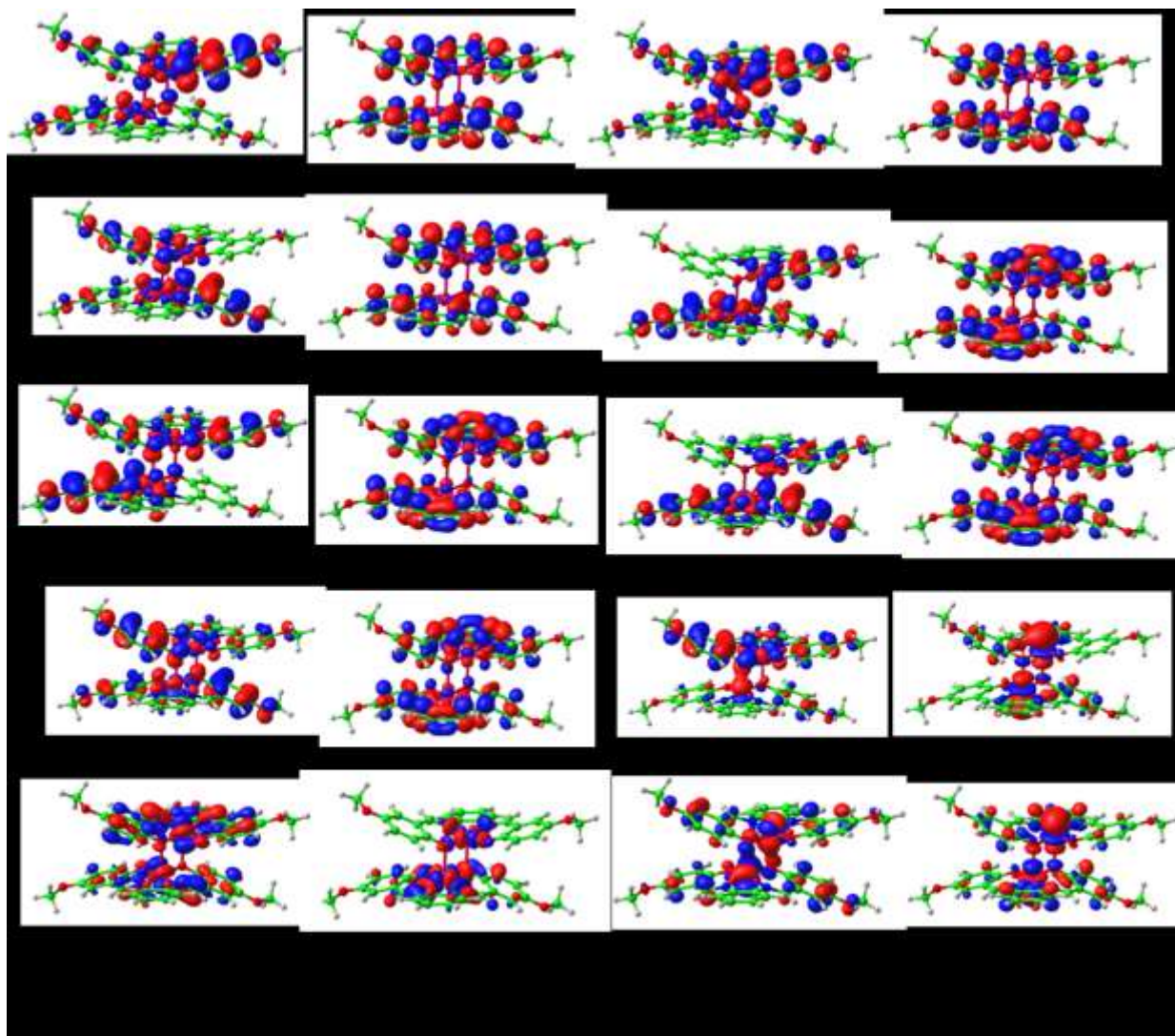


Figure S18: The molecular orbitals of CoL5 dimer in triplet spin state. The energies are in eV.

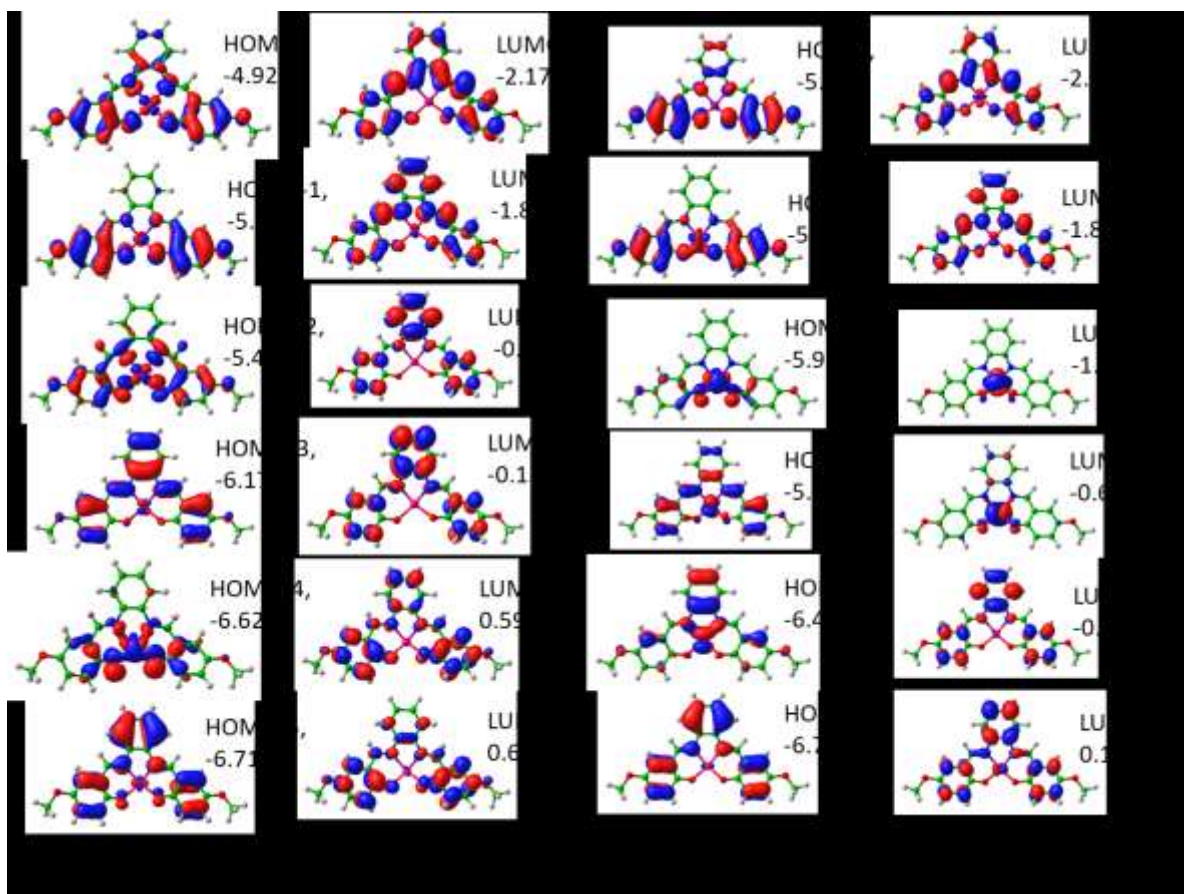


Figure S19: The molecular orbitals of CoL5, encapsulated and extracted in quartet spin state. The energies are in eV.

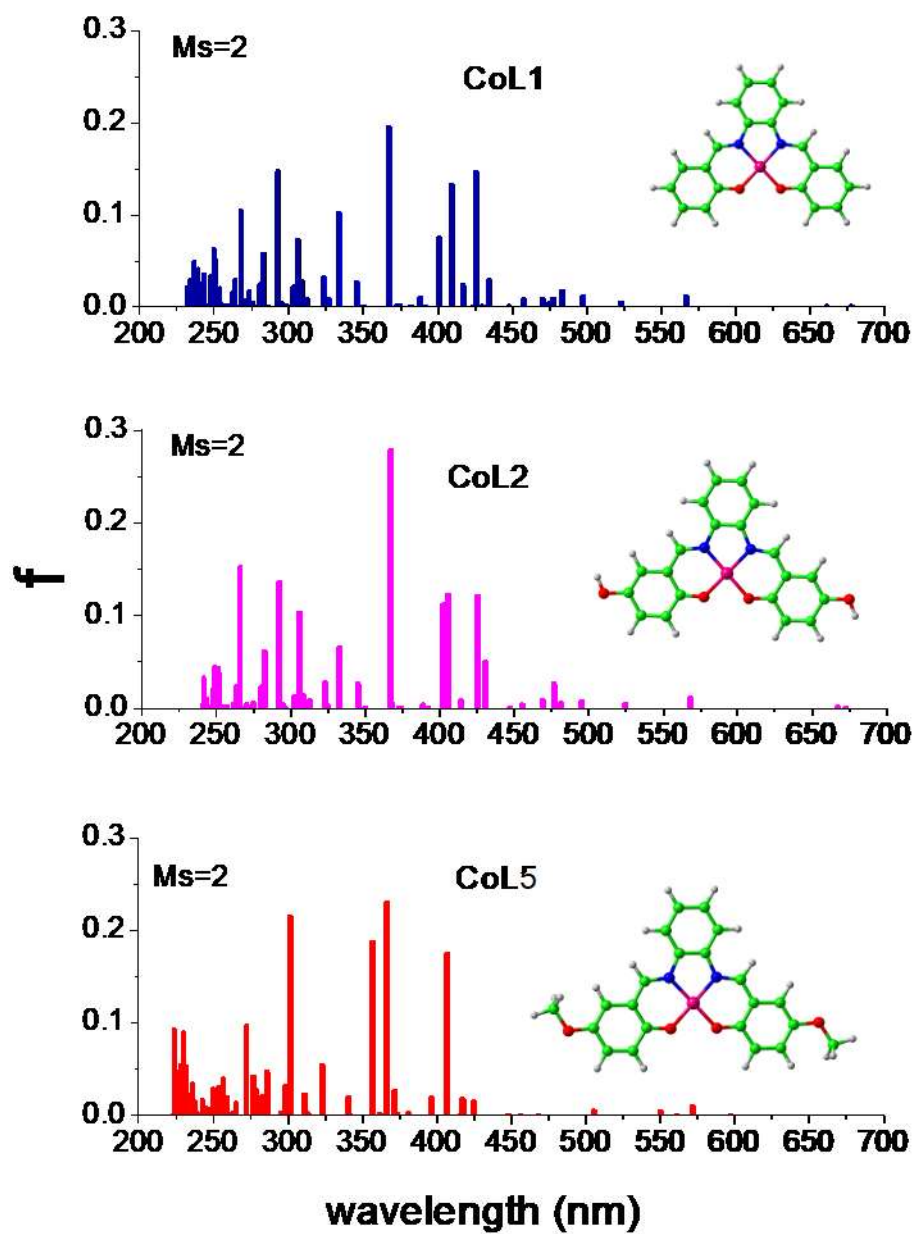


Figure S20: The TD-DFT spectra for dimeric, monomeric CoL1, CoL2 and CoL5. The optimized structures of CoL1, CoL2 and CoL5 are given in the respective insets.

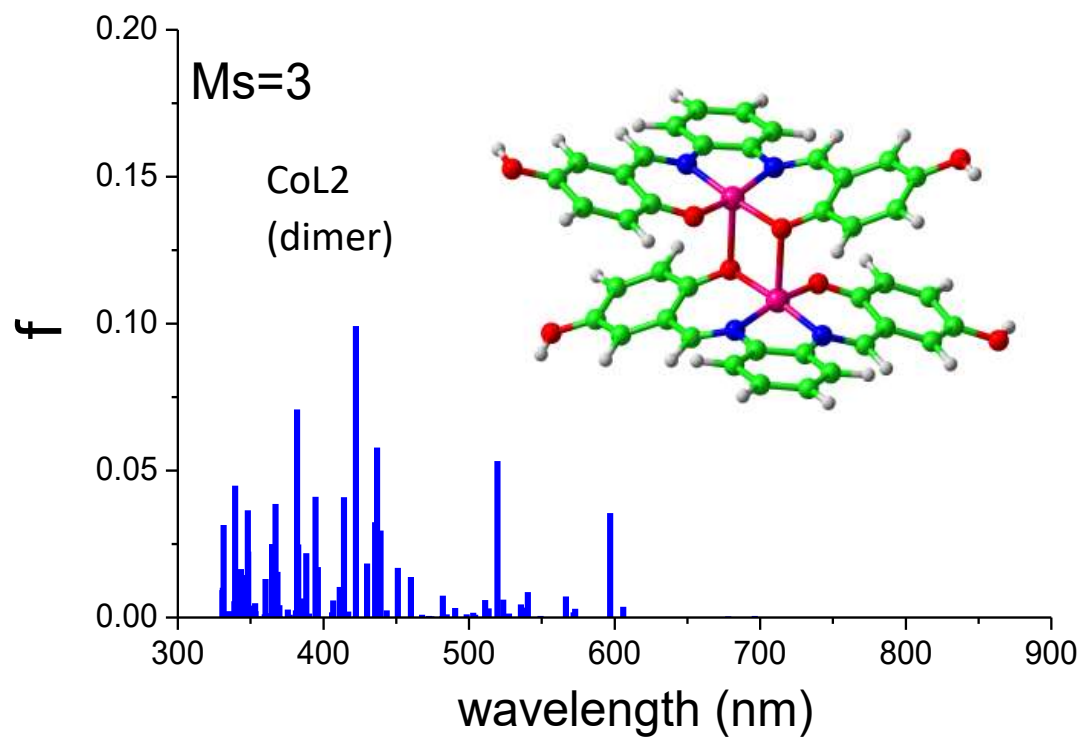


Figure S21: The TD-DFT spectra for CoL2 dimer in triplet state. The optimized structure is given in the inset.

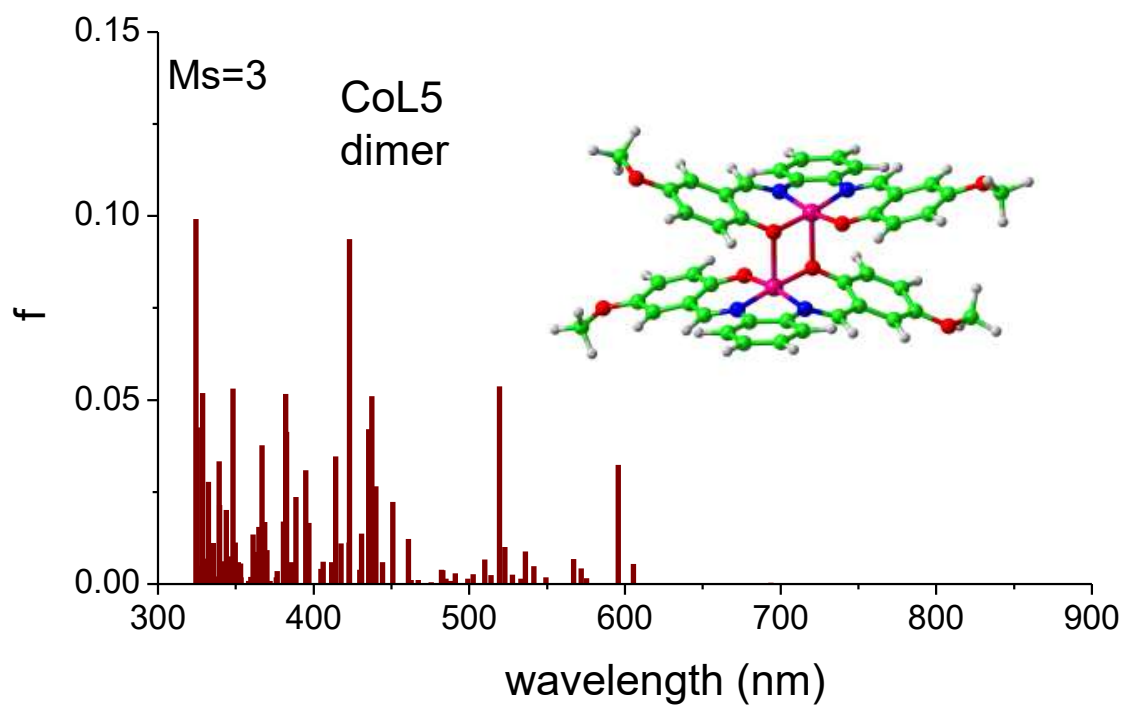


Figure S22: The TD-DFT spectra for CoL5 dimer in triplet state. The optimized structure is given in the inset.

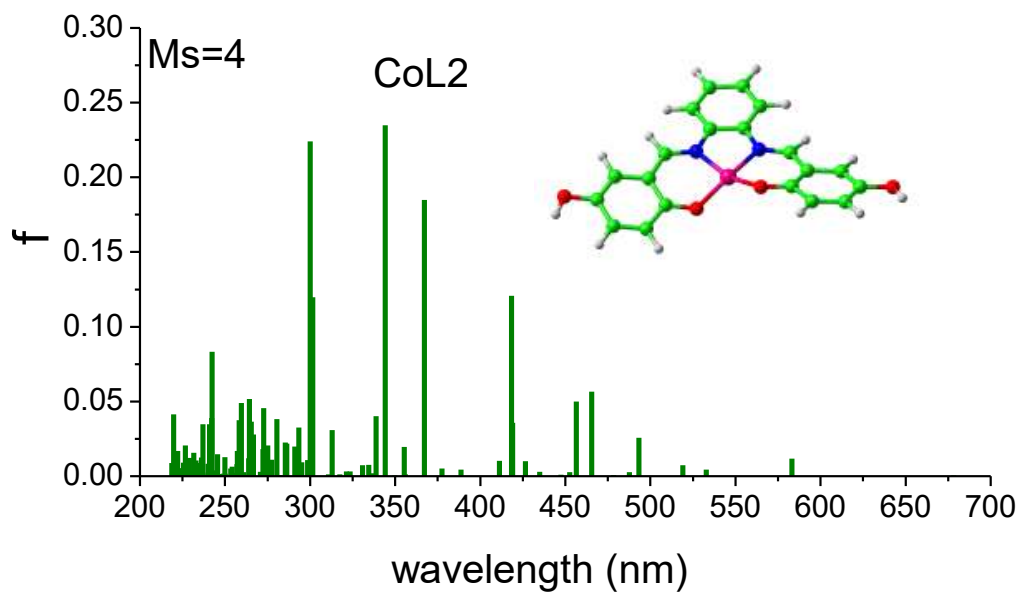


Figure S23: The TD-DFT spectra for CoL2 monomer in encapsulated and extracted quartet state. The optimized structure is given in the inset.

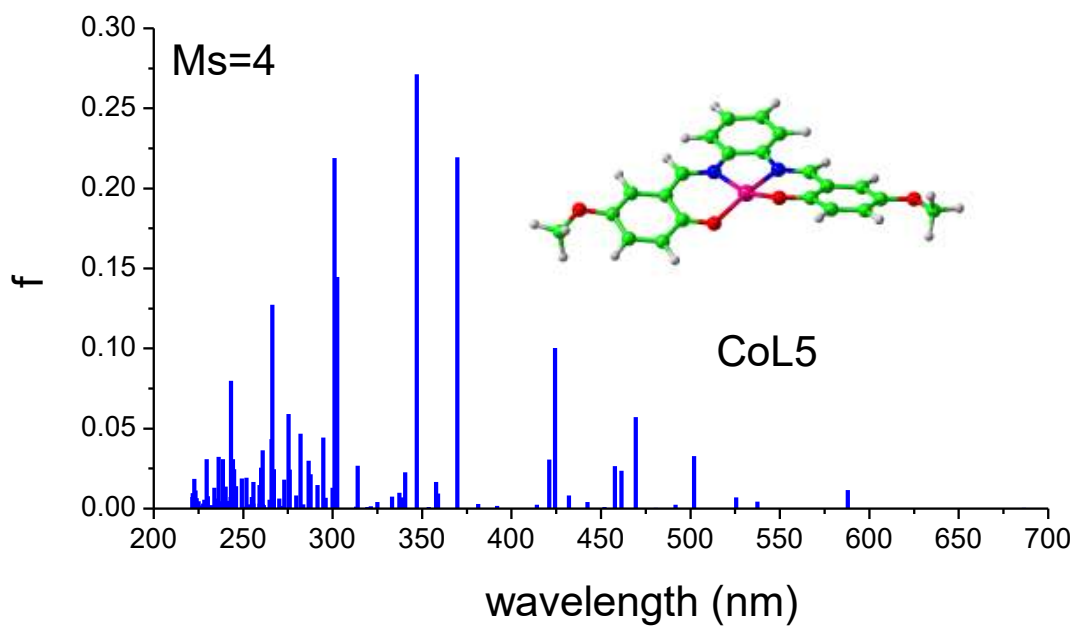


Figure S24: The TD-DFT spectra for CoL5 monomer in encapsulated and extracted quartet state. The optimized structure is given in the inset.

Table S5: Optimization of reaction condition for photocatalytic dye-degradation**(a) % degradation of rhodamine B after 1.5 h reaction time with H₂O₂ as oxidant**

S. No.	Catalyst	Amount of Catalyst (mmol)	% Degradation
1	CoL1-Y	0.0012	15.3
2	CoL1-Y	0.0024	20.3
3	CoL1-Y	0.0036	35.4

Reaction conditions: 0.02 mmol of 50 ml rhodamine B aqueous solution, H₂O₂ (0.66 mmol).**(b) % degradation of rhodamine B after 1.5 h reaction time with 0.0036 mmol of catalyst**

S. No.	Catalyst	H ₂ O ₂ (mmol)	% Degradation
1	CoL1-Y	0.22 mmol	15.2
2	CoL1-Y	0.44 mmol	20.5
3	CoL1-Y	0.66 mmol	35.4
4	CoL1-Y	0.88 mmol	60.5

Reaction conditions: 0.02 mmol of 50 ml rhodamine B aqueous solution, Amount of catalyst (0.0036 mmol).**(c) % degradation of rhodamine B by UV/ H₂O₂ alone.**

S. No.	Catalyst	Condition	% Degradation
1	CoL1-Y	UV	6.5
2	CoL1-Y	H ₂ O ₂	8.5

Reaction conditions: 0.02 mmol of 50 ml rhodamine B aqueous solution.**(d) % degradation of rhodamine B after 1.5 h reaction time in dark, visible-light and UV light.**

S. No.	Catalyst	Light condition	% Degradation
1	CoL1-Y	Dark	13.5
2	CoL1-Y	Visible	20.3
3	CoL1-Y	UV	60.5

Reaction conditions: 0.02 mmol of 50 ml rhodamine B aqueous solution, H₂O₂ (0.66 mmol). Amount of catalyst (0.0036 mmol).

Optimization of reaction condition for coupling of styrene oxide to CO₂

To get the optimized reaction condition, initially, CoL1 and CoL1-Y were used as the catalyst in the reaction. The activity was monitored using Gas Chromatography using bromobenzene as an internal standard. The calibration curve is given Figure S25. Initially, the reaction was carried out with styrene oxide (10 mmol, 1.2g), TBAB (0.05mmol, 16.1 mg), encapsulated complex (100 mg) using CO₂ at a pressure of 5 bar at 80 °C for 1.5 hours. We got a conversion of 66% and a TON of 622. By increasing the temperature to 100 °C, both the conversion and TON increased to 77% and 720, respectively. Inspired by the improvement in the activity, we further increased the temperature to 130 °C. But there was no betterment in the activity. We then tried the reaction in the best temperature conditions (5 bar, 130 °C and 1.5h) but with less catalyst loading of 50 mg. To our surprise, there was a significant improvement in TON from 718 to 1595. Encouraged by this result, we further decreased the amount of the catalyst to 25 mg and found that the TON increased even further to 2955 which we considered as the optimized reaction condition. We then tried the same reaction with neat complex at 130 °C with 0.05mmol of the complex and 0.05mmol of TBAB. We got a TON of 173 and upon further decreasing the catalyst and the cobalt-catalyst loading to 0.025mmol, the TON increased to 330. The increase in activity with decrease in the catalyst loading can be attributed to the site isolation provided by lesser amount of catalyst.

Table S6: Optimization of reaction condition of coupling of styrene oxide to CO₂

S. No	Catalyst	Temperature (°C)	Amount	Time (h)	TON	Conversion (%)
1	CoL1-Y	80	100 mg	1.5	622	66
2	CoL1-Y	80	50 mg	1.5	1438	76
3	CoL1-Y	100	50 mg	1.5	1515	81
4	CoL1-Y	100	100 mg	1.5	720	77
5	CoL1-Y	130	100 mg	1.5	718	76
6	CoL1-Y	130	50 mg	1.5	1595	85
7	CoL1-Y	130	25 mg	1.5	2955	79
8	CoL1	80	0.05 mmol	1.5	160	78
9	CoL1	80	0.025 mmol	1.5	300	72
10	CoL1	100	0.05 mmol	1.5	163	80
11	CoL1	100	0.025 mmol	1.5	306	76
12	CoL1	130	0.05 mmol	1.5	173	85
13	CoL1	130	0.025 mmol	1.5	330	82

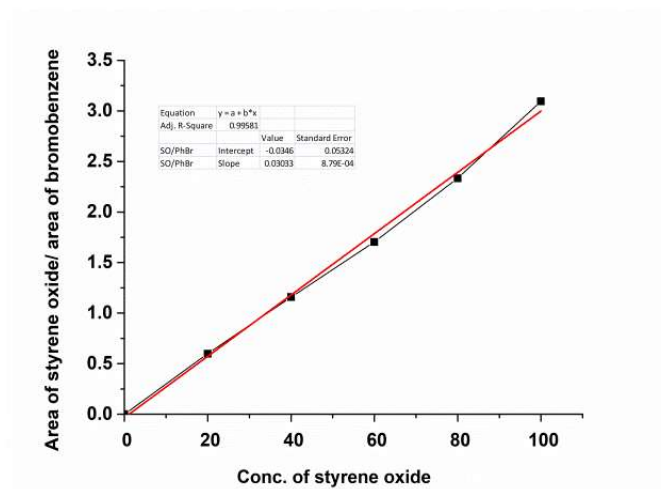


Figure S25: Calibration curve for styrene oxide.

References

1. H.-C. Zhang, W.-S. Huang and L. Pu, Biaryl-based macrocyclic and polymeric chiral (salophen) Ni (II) complexes: synthesis and spectroscopic study, *The Journal of organic chemistry*, 2001, **66**, 481-487.
2. A. P. Andrade, L. M. Arantes, J. Y. Kadooca, R. L. Carvalho, A. de Fatima and A. A. Sabino, Palladium complexes with tetradentate Schiff bases or their corresponding amines: synthesis and application in Heck reactions, *ChemistrySelect*, 2016, **1**, 886-890.
3. M. Salavati-Niasari, Synthesis and characterization of host (nanodimensional pores of zeolite-Y)-guest [unsaturated 16-membered octaaza-macrocycle manganese (II), cobalt (II), nickel (II), copper (II), and zinc (II) complexes] nanocomposite materials, *Chemistry letters*, 2005, **34**, 1444-1445.
4. Y. Yang, H. Ding, S. Hao, Y. Zhang and Q. Kan, Iron (III), cobalt (II) and copper (II) complexes bearing 8-quinolinol encapsulated in zeolite □ Y for the aerobic oxidation of styrene, *Applied Organometallic Chemistry*, 2011, **25**, 262-269.
5. K. K. Bania, D. Bharali, B. Viswanathan and R. C. Deka, Enhanced catalytic activity of zeolite encapsulated Fe (III)-Schiff-base complexes for oxidative coupling of 2-naphthol, *Inorganic chemistry*, 2012, **51**, 1657-1674.
6. A. Oyinade, A. S. Kovo and P. Hill, Synthesis, characterization and ion exchange isotherm of zeolite Y using Box-Behnken design, *Advanced Powder Technology*, 2016, **27**, 750-755.
7. M. S. Hosseini Hashemi, F. Eslami and R. Karimzadeh, Organic contaminants removal from industrial wastewater by CTAB treated synthetic zeolite Y, *Journal of Environmental Management*, 2019, **233**, 785-792.

8. S. Rayalu, S. U. Meshram and M. Z. Hasan, Highly crystalline faujasitic zeolites from flyash, *Journal of Hazardous Materials*, 2000, **77**, 123-131.
9. M. Maurya, S. Titinchi, S. Chand and I. Mishra, Zeolite-encapsulated Cr (III), Fe (III), Ni (II), Zn (II) and Bi (III) salpn complexes as catalysts for the decomposition of H₂O₂ and oxidation of phenol, *Journal of Molecular Catalysis A: Chemical*, 2002, **180**, 201-209.
10. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 09, Revision A.02; Gaussian Inc, Wallingford, CT, 2009.
11. A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *The Journal of Chemical Physics*, 1993, **98**, 5648-5652.
12. A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Physical Review A*, 1988, **38**, 3098-3100.
13. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, *Physical Review B*, 1992, **46**, 6671-6687.
14. J. P. Perdew, in *Electronic Structure of Solids* ed. P. Z. a. H. Eschrig, Akademie Verlag, Berlin, 1991, p. 11.
15. A. Choudhary, B. Das and S. Ray, Encapsulation of a Ni salen complex in zeolite Y: an experimental and DFT study, *Dalton Transactions*, 2015, **44**, 3753-3763.

16. A. Choudhary, B. Das and S. Ray, Encapsulated Schiff base nickel complex in zeolite Y: Correlation between catalytic activities and extent of distortion supported by experimental and DFT studies, *Inorganica Chimica Acta*, 2017, **462**, 256-265.
17. S. Kumari, B. Das and S. Ray, An insight into the catalytic activity of palladium Schiff-base complexes towards the Heck coupling reaction: routes via encapsulation in zeolite-Y, *Dalton Transactions*, 2019, **48**, 15942-15954.
18. S. Kumari, K. Maddipoti, B. Das and S. Ray, Palladium–Schiff Base Complexes Encapsulated in Zeolite-Y Host: Functionality Controlled by the Structure of a Guest Complex, *Inorganic Chemistry*, 2019, **58**, 1527-1540.