Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Chromogenic Detection of the xylene isomers and Luminogenic Chemosensing of the *o*-xylene Employing a New Macrocyclic Cobalt Complex: Synthesis, X-ray Crystallographic, Spectroscopic and Computational Studies

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Table S1. Materials used for sensing xylene

scientific group	synthesized system	xylene isomer
Tang et al[15]	TPE-β-CD nanosheets	*p*-xylene
Mèçabih[16]	Fe, Fe−Al pillared clay	benzene, toluene, and *o*-xylene
Zhang et al[17]	pillar[5]arene (WP5)	*o*-xylene and *p*-xylene
Lee et al[18]	$NiO/NiMoO_4$ nanocomposite	*p*-xylene
Harrison et al[19]	$[Co_4(\mathbf{1})_2]^{8-}$	*p*-xylene
Bej et al[10]	PSP-CMERI-1 PSP-CMERI-2	*m*-xylene
Yuxi Yang et Al[20]	MIL-53(Al)	*o*-xylene and *p*-xylene
Zhao et al[11]	NUS-40	*o*-xylene
Rosales-Vázquez et al[13]	$[Zn_2(\mu_2\text{-BDC})_2(iQ)_2]_\infty$	*p*-xylene
Ono et al[12]	NDI with a 2-benzophenone unit	toluene, *p*-xylene, 4-fluorotoluene, and anisole
Zhang et al[21]	(P(VBC-co-MMA)-SiO_2IOPC).	*o*-xylene, *m*-xylene and *p*-xylene
Present work	$Co_2(\mathbf{2py})_2Cl_4$**.** DMF	*o*-xylene, *m*-xylene and *p*-xylene

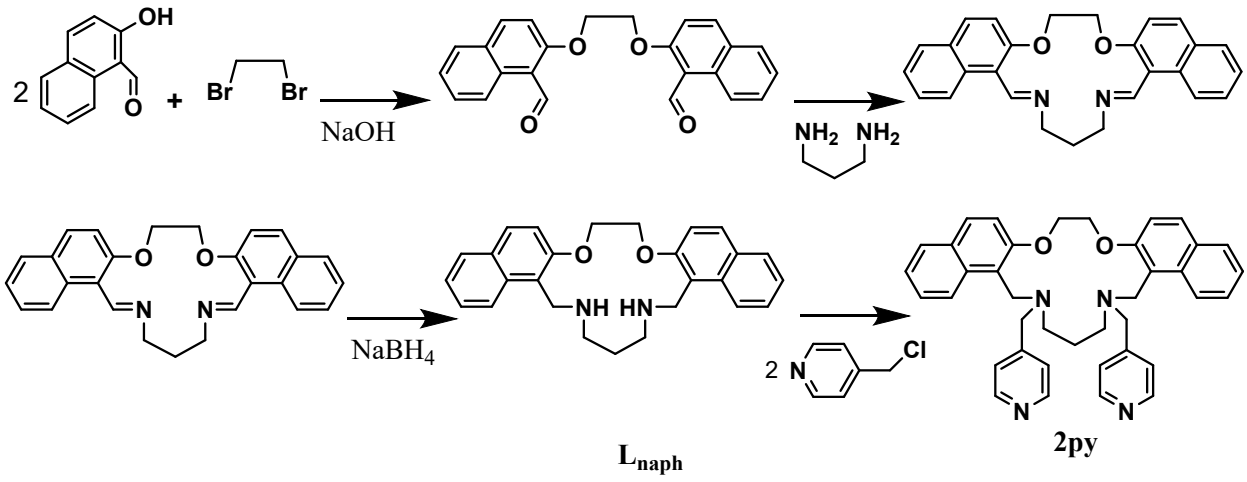

Figure S1 The synthetic route of new ligand **2py**

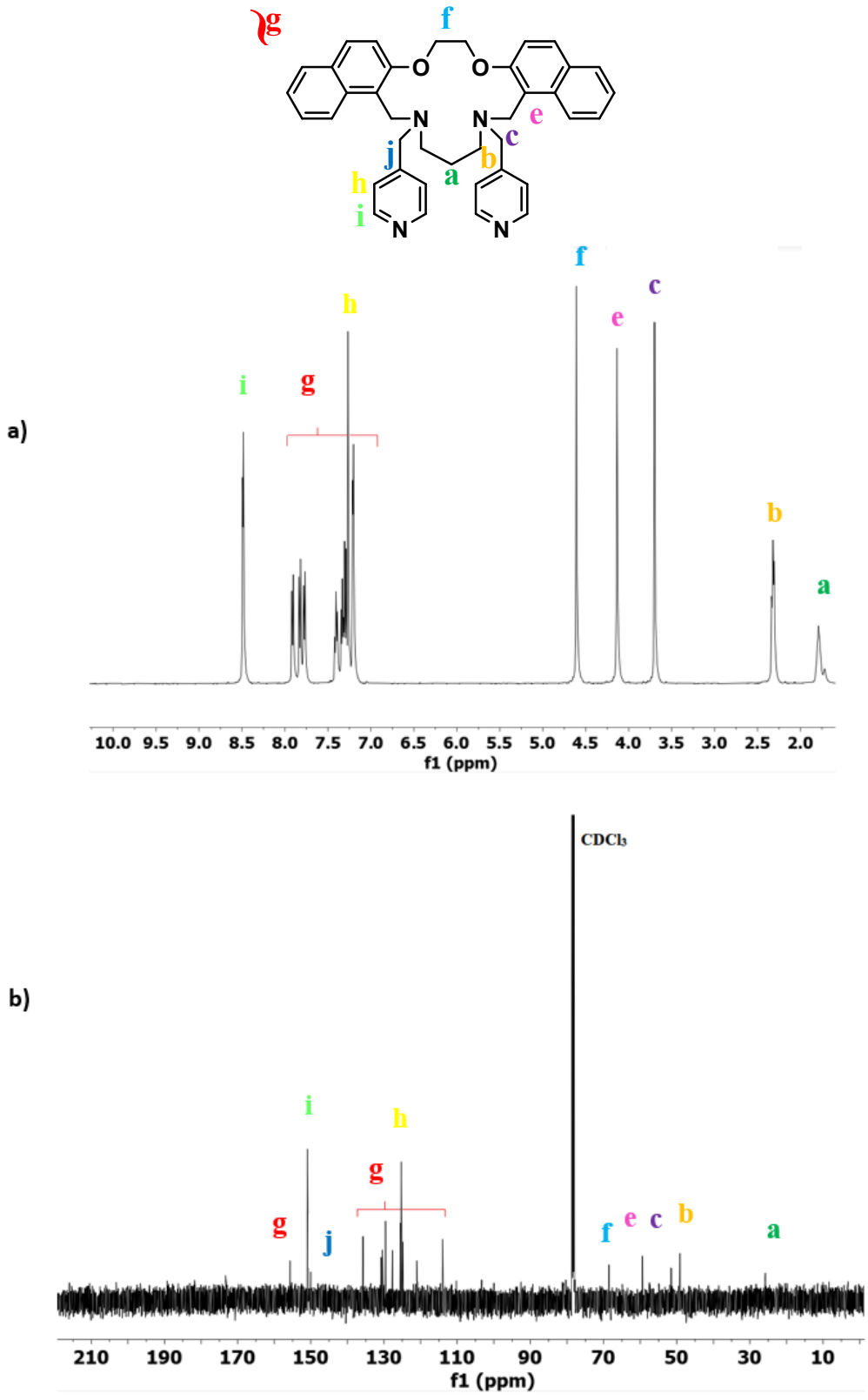

Figure S2 a) ^{1}H NMR and b) ^{13}C NMR spectra of **2py** along with assignment

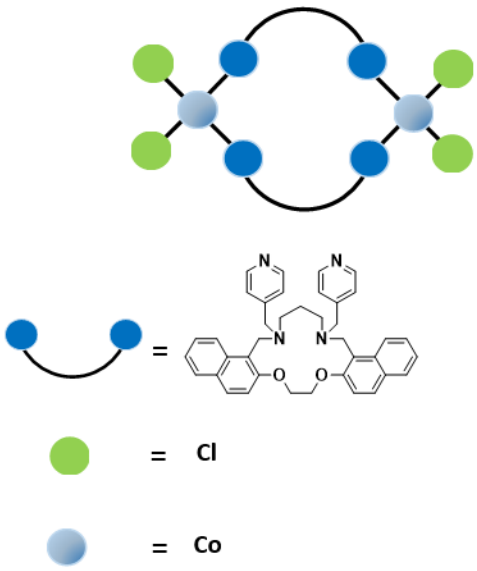

Figure S3 Illustrative representation for the formation of Co_2(**2py**)$_2Cl_4$ dimer

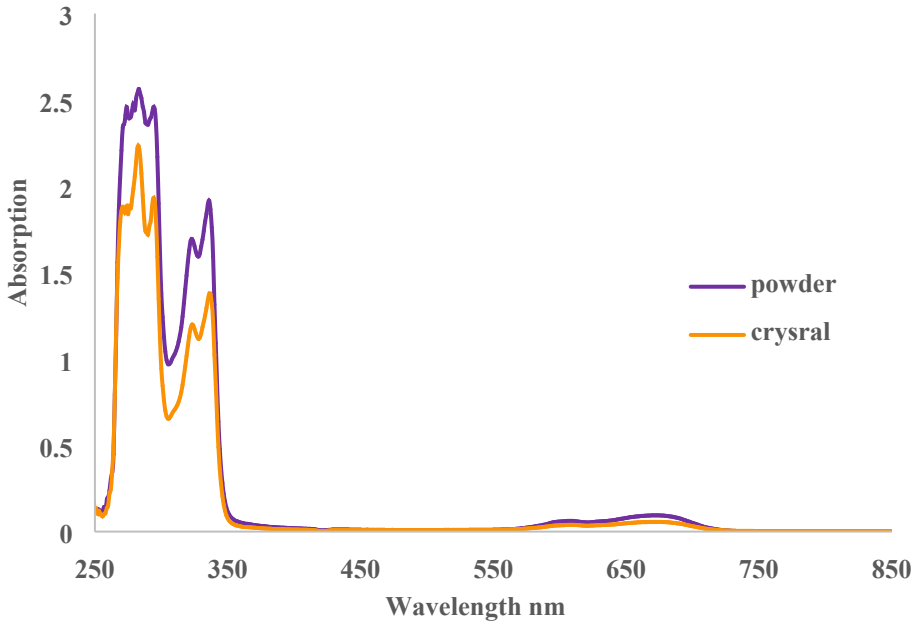

Figure S4 The UV-vis spectra of Co_2(**2py**)$_2Cl_4$ powder and crystal in DMF at 298K

Table S2 The data collection, structure refinement and the crystal data for $Co_2(\mathbf{2py})_2Cl_4$. DMF

Compound	$Co_2(\mathbf{2py})_2Cl_4$. DMF
Empirical formula	$C_{78}H_{76}Cl_4Co_2N_8O_4 \cdot 2(C_{1.5}H_{3.5}N_{0.5}O_{0.5})$
M_r	1522.22
Temperature (K)	290
Wavelength (Å)	0.7073
Crystal system	Triclinic
Space group	Pī
a, b, c (Å)	9.869(2), 10.238 (2), 18.824 (4)
α, β, γ (deg)	90.35(3), 94.07(3), 94.06(3)
Volume (Å^3)	1892.2(7)
Z	1
Radiation type	Mo $K\alpha$
Crystal size (mm)	0.4 × 0.3 × 0.25
T_{min}, T_{max}	0.991, 1.011
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11825, 6053, 5647
R_{int}	0.020
D_{calc} (Mg/m^3)	1.336
μ(mm^{-1})	0.637
F(000)	794.0
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.114, 1.08
No. of reflections	6053
No. of parameters	470
No. of restraints	17
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.23

Table S3 The Co–N and Co–Cl bond lengths (Å) and angles (°) in Co_2(**2py**)$_2Cl_4$. DMF

Co(3)-Cl(1)	2.223(1)
Co(3)-Cl(2)	2.241(1)
Co(3)-N(7)	2.309(2)
Co(3)-N(6)	2.036(2)
Cl(1)-Co(3)-Cl(2)	120.06(3)
N(6)-Co(3)-N(7)	104.08(8)
N(6)-Co(3)- Cl(2)	106.24(6)
N(6)-Co(3)- Cl(1)	111.46(6)
N(7)- Co(3)- Cl(2)	108.68(6)
N(7)- Co(3)- Cl(1)	105.21(6)

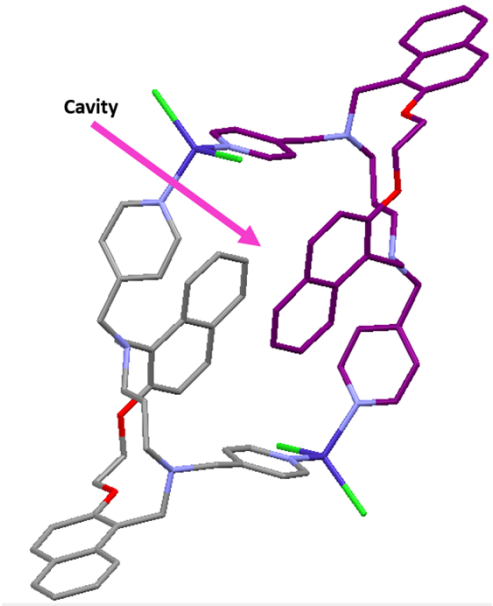

Figure S5 The representation of the cavity of the Co_2(**2py**)$_2Cl_4$. DMF (hydrogen atoms and DMF molecule were omitted for clarity)

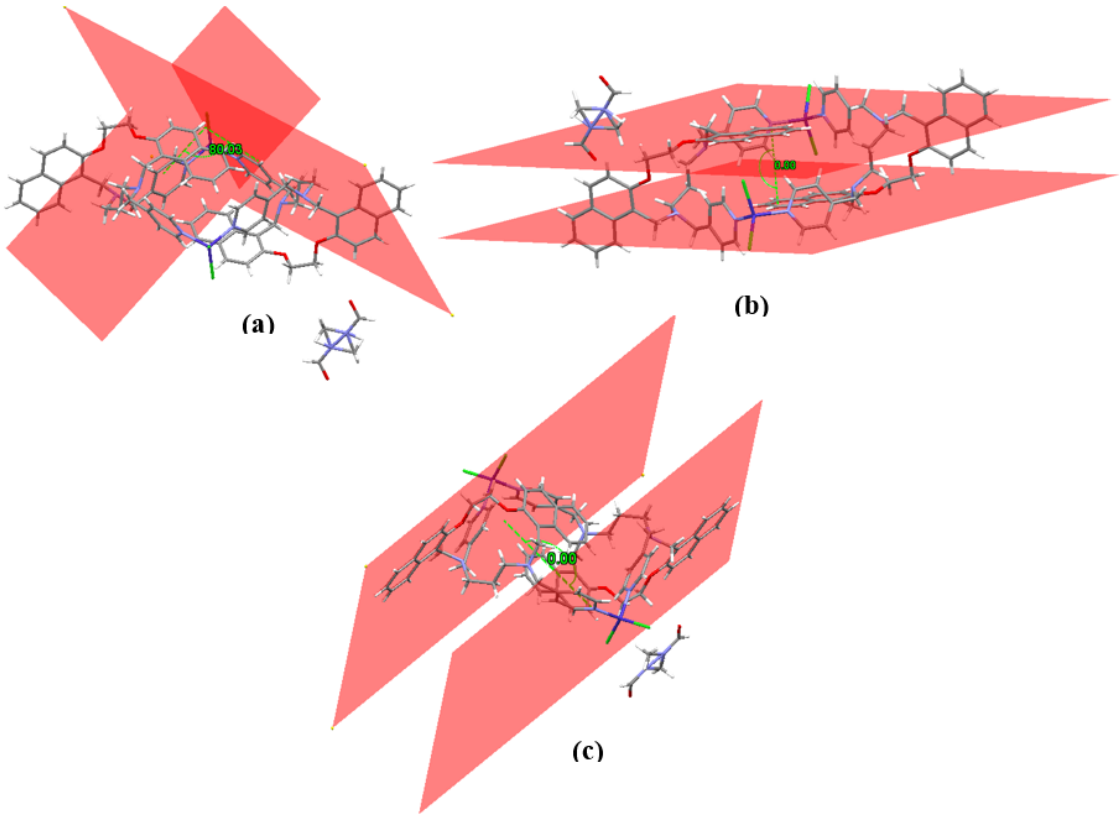

Figure S6 a) The dihedral angle between two pyridine moieties, b) The dihedral angle between two naphthalene rings oriented the inward of the molecule, c) The dihedral angles between two naphthalene rings oriented outward of the molecule

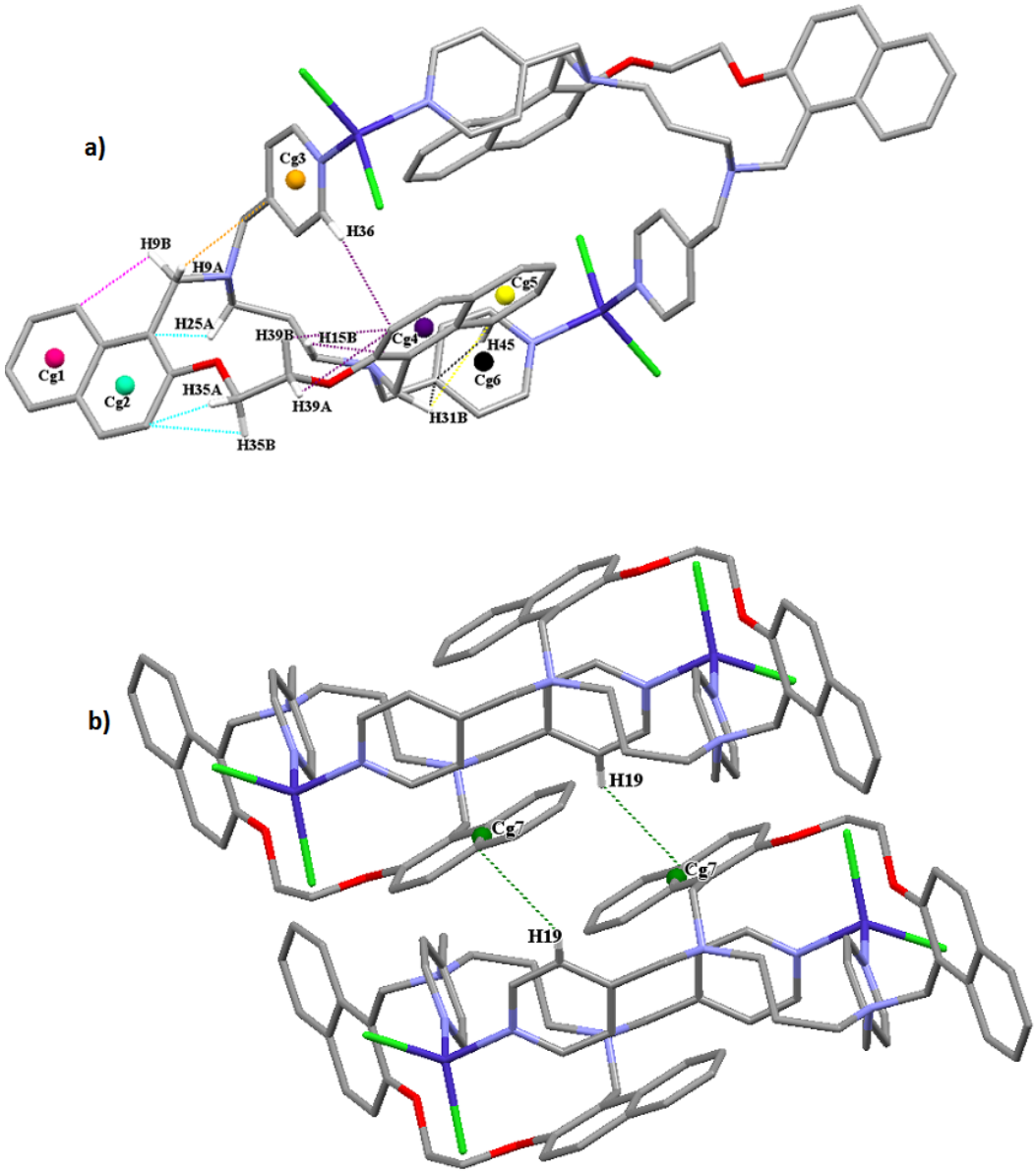

Figure S7 The representation of the (a) intramolecular C−H…Cg interactions b) intermolecular C−H…Cg interactions in Co_2(**2py**)$_2Cl_4$. DMF (only relevant hydrogen atoms are shown and the interactions with one Cg are displayed with the same dash line color for clarifying)

Table S4 Weak interactions data (°, Å) in $Co_2(\mathbf{2py})_2Cl_4$. DMF, Cg stands for (the middle point of) the six and ten member rings

Analysis of Potential Hydrogen Bonds						
D	H	A	D−H	H···A	D···A	D−H···A
C40	H40	O4	0.93	2.542	3.438	161.84
C15	H15B	O4	0.97	2.597	3.315	130.94
C31	H31A	O4	0.97	2.380	2.791	104.88
C35	H35A	O3	0.97	2.641	3.550	156.16
C9	H9A	O1	0.97	2.556	2.723	89.36
D	H	A	D−H	H···A	D···A	D−H···A
C15	H15B	N2	0.97	2.622	3.009	104.07
C18	H18	N2	0.93	2.564	2.874	99.92
Analysis of X−H···C Interactions						
C	H	X	C−H	H···X	C···X	C−H···X
C14	H14B	Cl1	0.97	2.746	3.612	149.11
C39	H39A	Cl1	0.97	2.713	3.589	150.52
C8	H8A	Cl2	0.97	2.934	3.810	150.82
Analysis of C−H···Cg(Pi-Ring) Interactions						
C−H		Cg	H···Cg	C−H···Cg	C···Cg	C−H, Pi
C9	–H9B	Cg1	3.688	94.88	3.892	108.79
C35	–H35A	Cg2	3.782	79.25	3.674	79.61
C35	–H35B	Cg2	3.739	78.67	3.674	87.43
C25	–H25A	Cg2	3.213	134.53	3.954	109.95
C9	–H9A	Cg3	3.673	117.68	4.212	97.73
C36	–H36	Cg4	3.212	126.46	3.839	147.05
C39	–H39A	Cg4	3.914	69.21	3.683	77.61
C39	–H39B	Cg4	3.641	84.84	3.683	88.56
C15	–H15B	Cg4	3.382	120.32	4.394	103.56
C31	–H31B	Cg5	3.794	88.75	3.852	95.22
C31	–H31B	Cg6	3.750	115.06	4.252	102.43
C45	–H45	Cg6	2.935	156.85	3.808	167.97
C19	–H19	Cg7	2.903	131.14	3.584	137.30

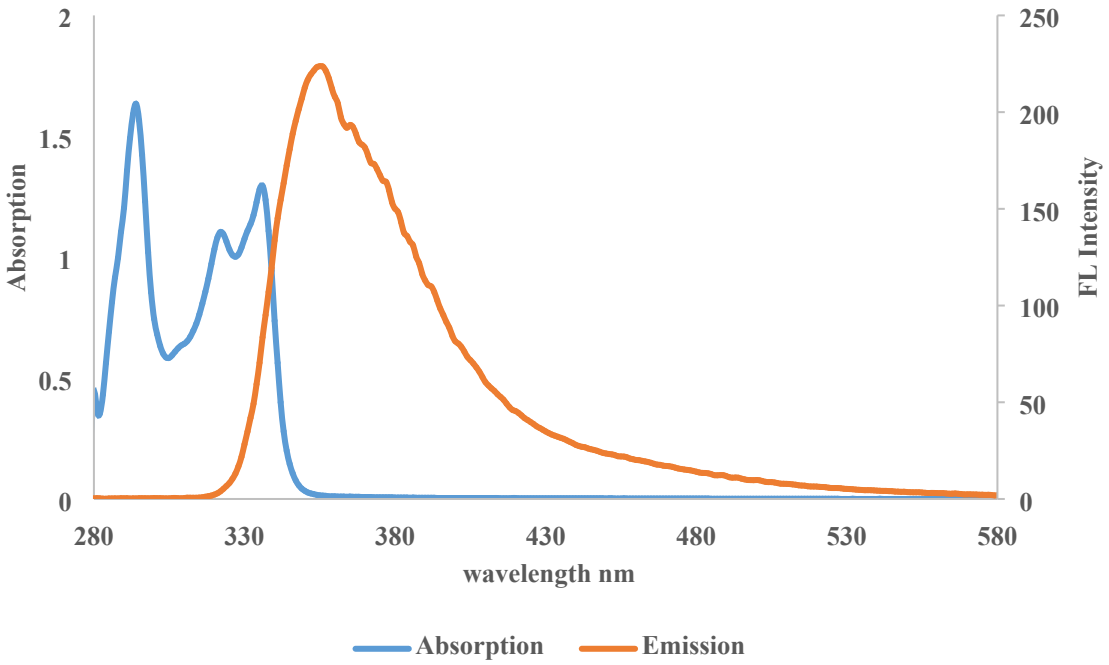

Figure S8 The absorption (blue line) and FL bands (orange line) of **2py** in ethanol at 298K ($\lambda_{excitation}$ 340 nm)

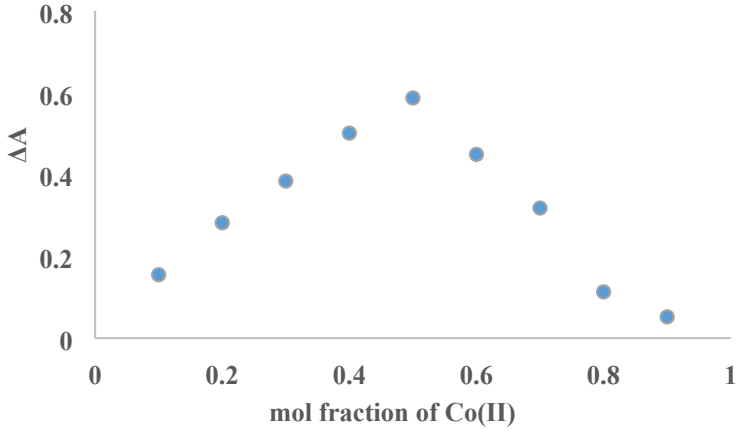

Figure S9 The Job's plots for Co(II)/**2py**

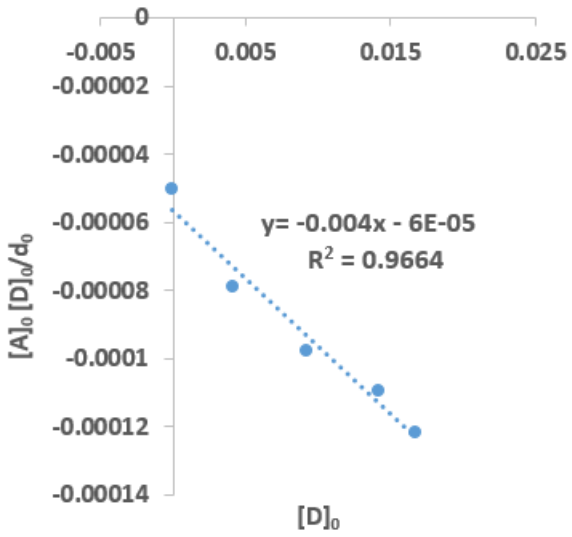

Figure S10 The Benesi-Hildebrand plot of Co(II)/**2py** in DMF at 298K

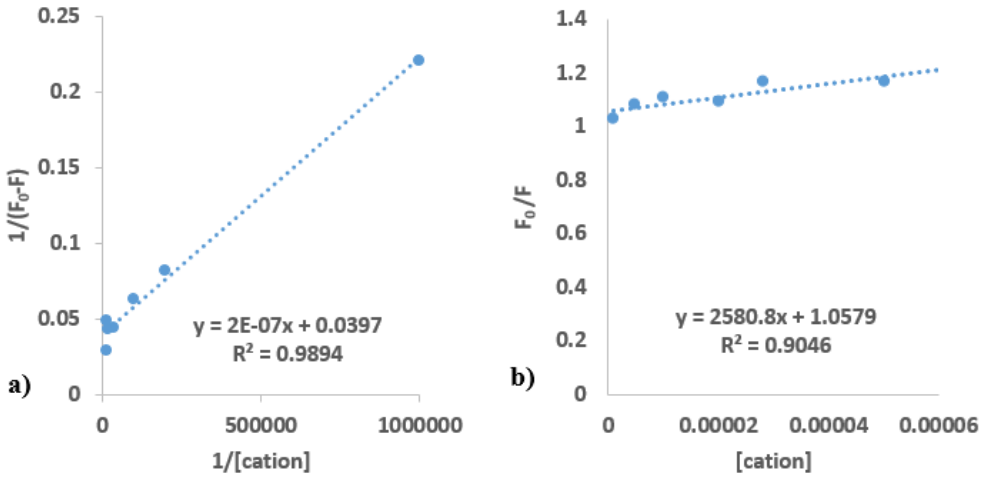

Figure S11 a) The Benesi-Hildebrand plot of Co(II)/**2py** and b) The Stern-Volmer plot of Co(II)/**2py**$_{\mathbf{naph}}$

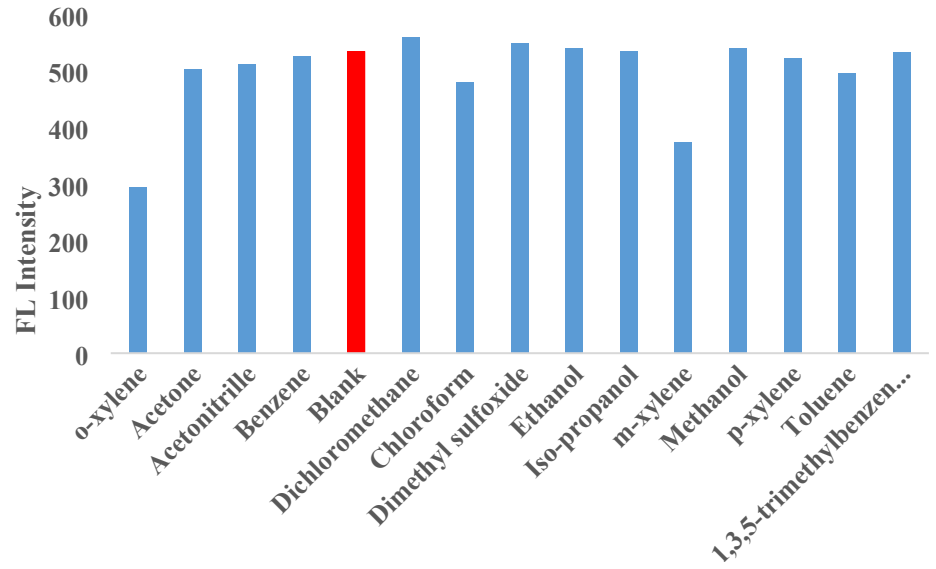

Figure S12 The FL emission intensities of Co_2(**2py**)$_2Cl_4$ in different organic solvent/DMF mixtures, see the text for description.

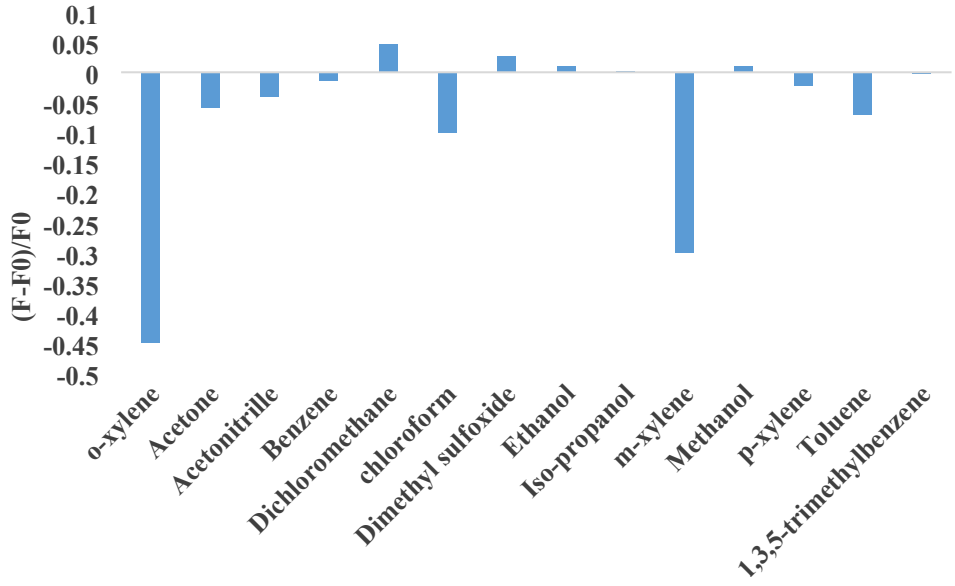

Figure S13 The FEF diagram of Co_2(**2py**)$_2Cl_4$ in DMF/solvent mixtures

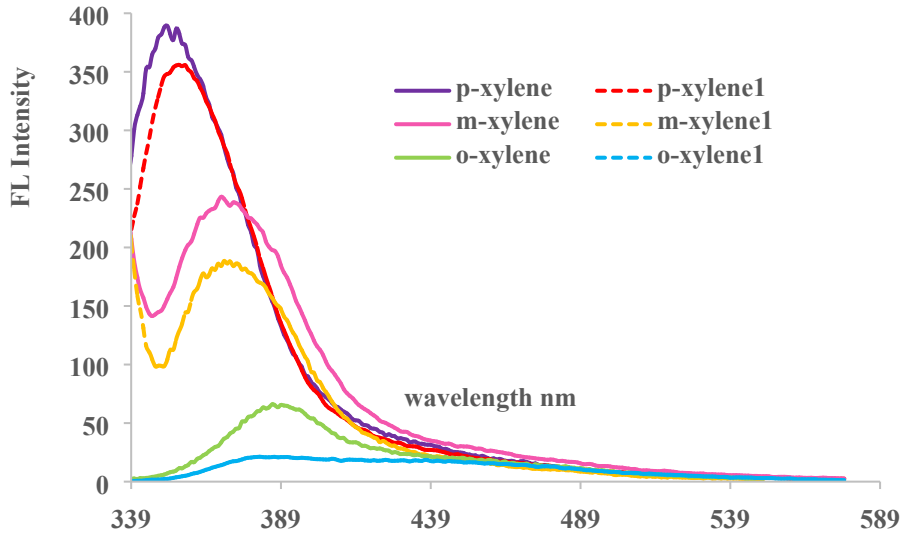

Figure S14 Comparative FL spectra of Co_2(**2py**)$_2Cl_4$ (0.33 mg mL^{-1}), dispersed in xylene isomers on day 1 (*o*-xylene, *m*-xylene, and *p*-xylene) *versus* 1 week (*o*-xylene1, *m*-xylene1, and *p*-xylene1)

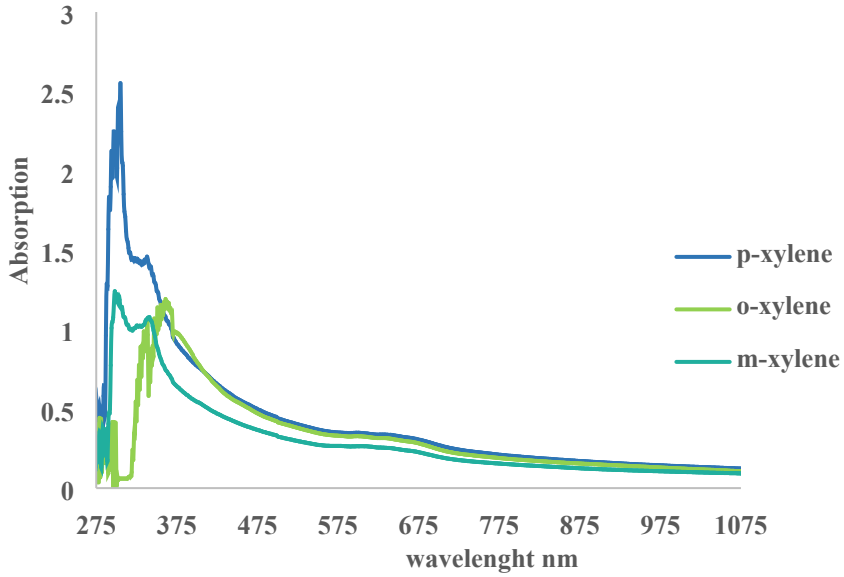

Figure S15 The UV-vis of Co_2(**2py**)$_2Cl_4$ (0.033 mg mL^{-1}) dispersed in *o-, m-* and *p*-xylene isomers

Table S5 The K_{FL} and K_{SV} of Co_2(**2py**)$_2Cl_4$ (1.4×10^{-5} M) with xylene isomers in DMF at 298 K

K_i value (M^{-1})	*o*-xylene	*m*-xylene	*p*-xylene
K_{FL}	$1.700\times10^6(\pm7715.79)$	$8.800\times10^5(\pm5874)$	$5.125\times10^3(\pm51.25)$
K_{SV}	$8.657\times10^2(\pm19.49)$	$4.615\times10^2(\pm6.84)$	$1.790\times10^3(\pm14.45)$

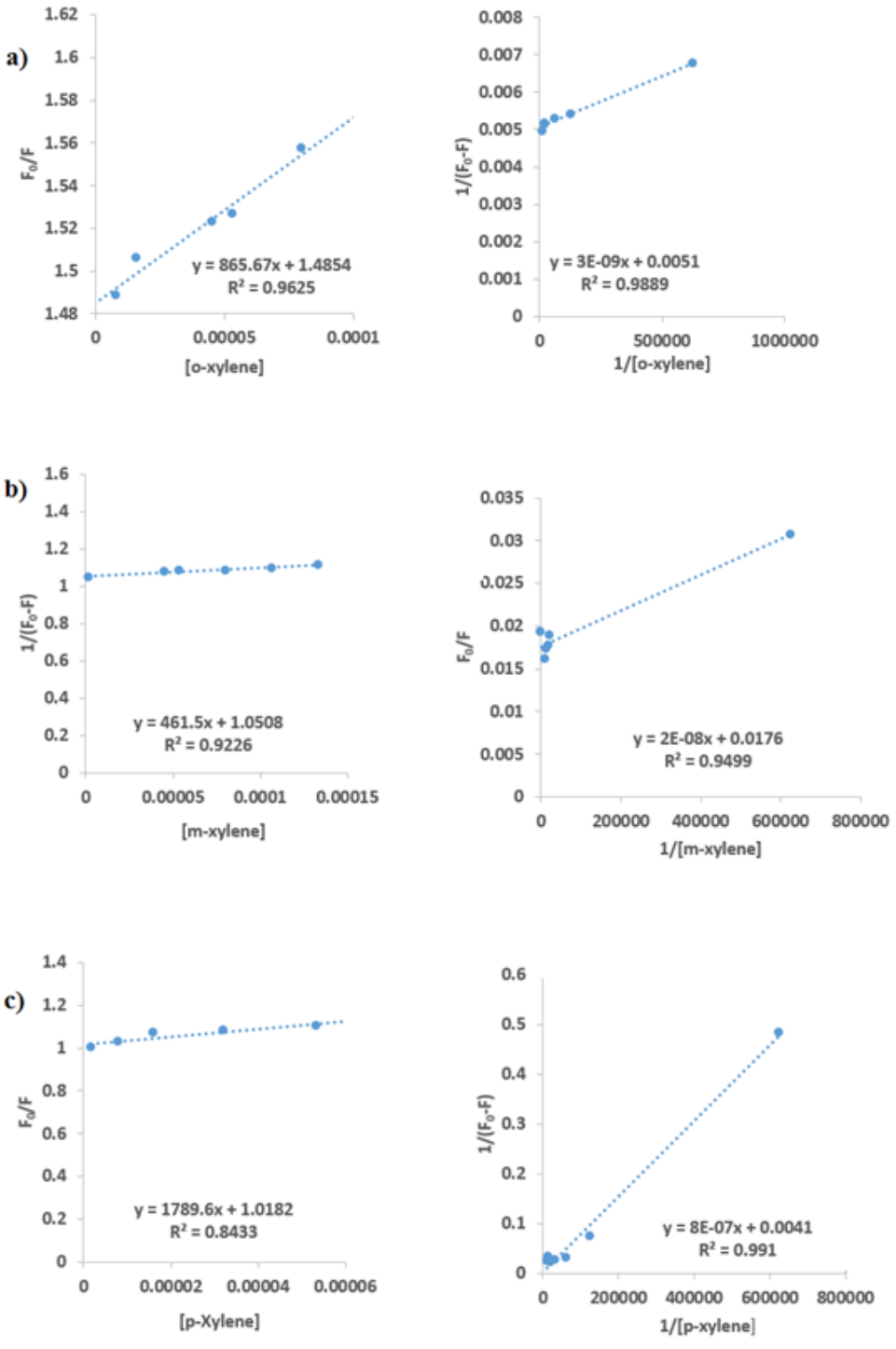

Figure S16 The Stern-Volmer plots (left column) and the Benesti-Hildbrand plots (right column) of Co_2(**2py**)$_2Cl_4$ /*o*-, *m*-, *p*-xylene

Table S6 The detected species by GC-Mass with their corresponding retention time (RT) (ox-2, mx-2,px-2 refers to the xylene after catalytic treatment

***o*-xylene**	
retention time (min)	compound
3.62-5.01	xylene
5.66	methylethyl-benzene
15.72	2-methyl-benzaldehyde
17.03	2-methyl-benzenemethanol
17.81	2-methyl-benzaldehyde
ox-2	
3.55-4.48	xylene
5.43	methylethyl- benzene
15.77	2-methyl-benzaldehyde
17.35	1-methoxymethyl-2-methylbenzene
17.**96**	2-methyl-benzoic acid
17.08	2-methyl-benzenemethanol
***m*-xylene**	
3.29	1,3-bis(3-phenoxyphenoxy)-benzene
4.11	ethyl-benzene
4.68 and 5.25	xylene
mx-2	
4.21 and 4.32	ethyl-benzene
4.64-5.73	xylene
13.29	4-methyl-benzaldehyde

***p*-xylene**	
Retention time (min)	Compound
3.86-4.42	xylene
px-2	
3.75-4.56	xylene

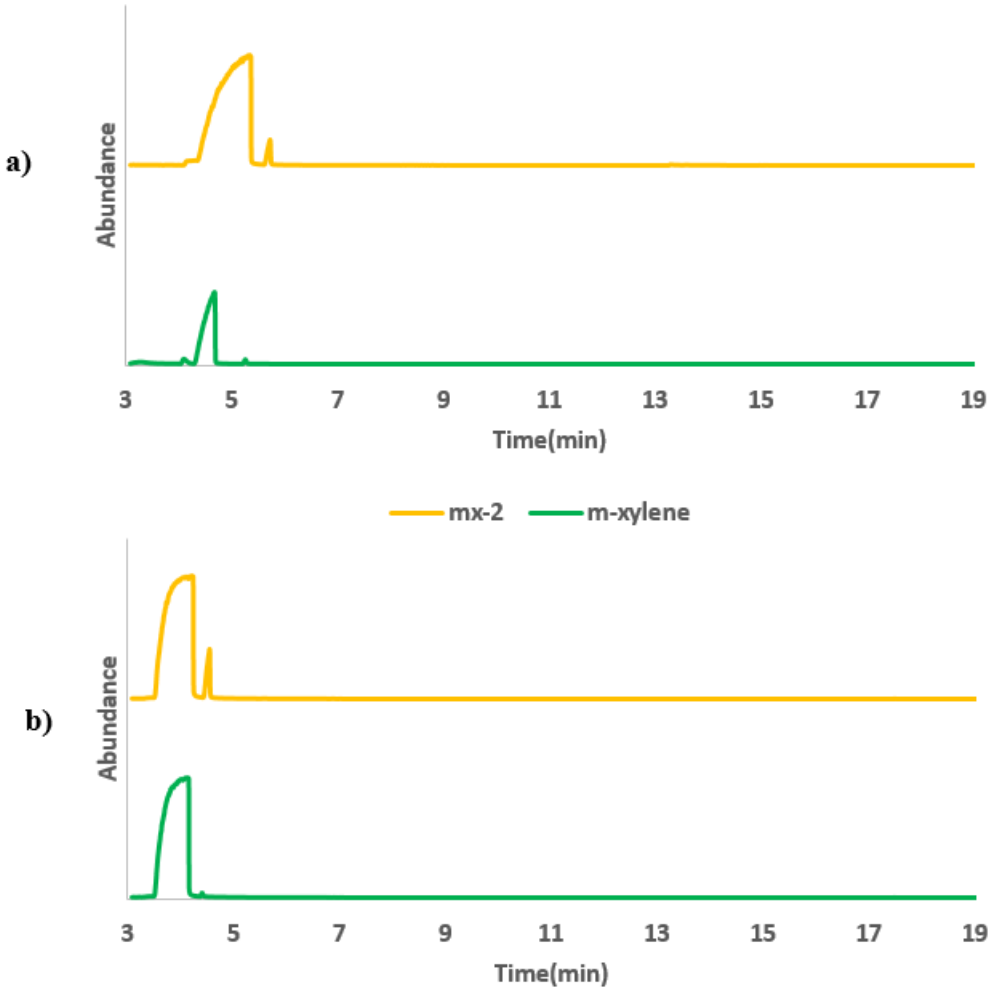

Figure S17 a) The GC-mass diagrams of: (a) *m*-xylene and mx-2 before and after catalytic treatment with Co_2(**2py**)$_2Cl_4$, respectively; b) *p*-xylene and px-2 before and after catalytic treatment with Co_2(**2py**)$_2Cl_4$, respectively.

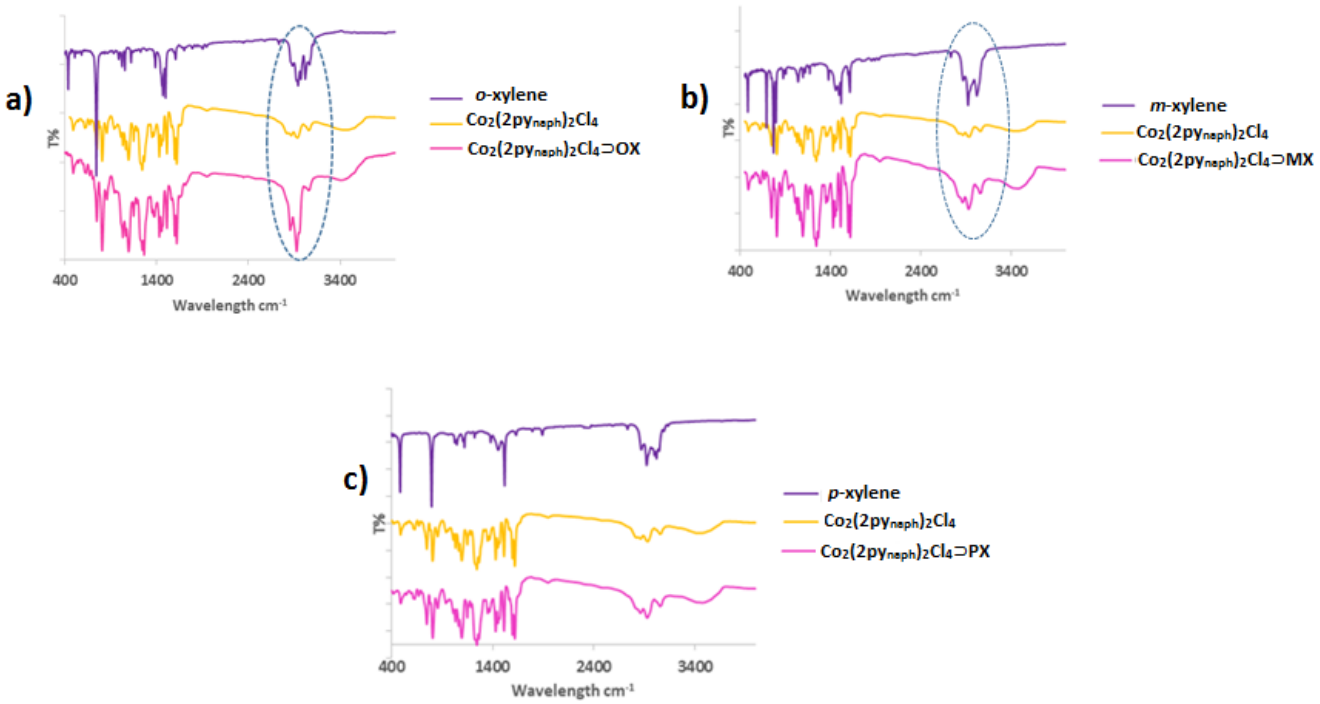

Figure S18 The FT-IR spectra of $Co_2(\mathbf{2py})_2Cl_4$ and a) *o*-xylene and $Co_2(\mathbf{2py})_2Cl_4\supset$OX, b) *m*-xylene and $Co_2(\mathbf{2py})_2Cl_4\supset$MX, c) *p*-xylene and $Co_2(\mathbf{2py})_2Cl_4\supset$PX.

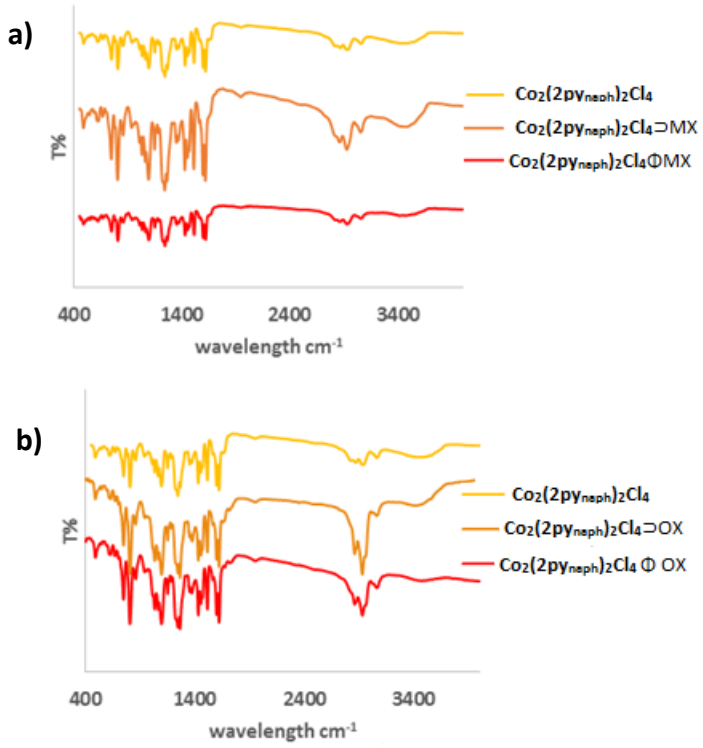

Figure S19. The FT-IR spectra of a) $Co_2(\mathbf{2py})_2Cl_4$ along with: a) $Co_2(\mathbf{2py})_2Cl_4$ ⊃MX, and $Co_2(\mathbf{2py})_2Cl_4$ ΦMX. ($Co_2(\mathbf{2py})_2Cl_4$ ΦOX and $Co_2(\mathbf{2py})_2Cl_4$ ΦMX refer to $Co_2(\mathbf{2py})_2Cl_4$ ⊃OX and $Co_2(\mathbf{2py})_2Cl_4$ ⊃MX, b) $Co_2(\mathbf{2py})_2Cl_4$ ⊃OX and $Co_2(\mathbf{2py})_2Cl_4$ ΦOX, respectively after exposure to the vacuum at 333K for 8h to release xylene).

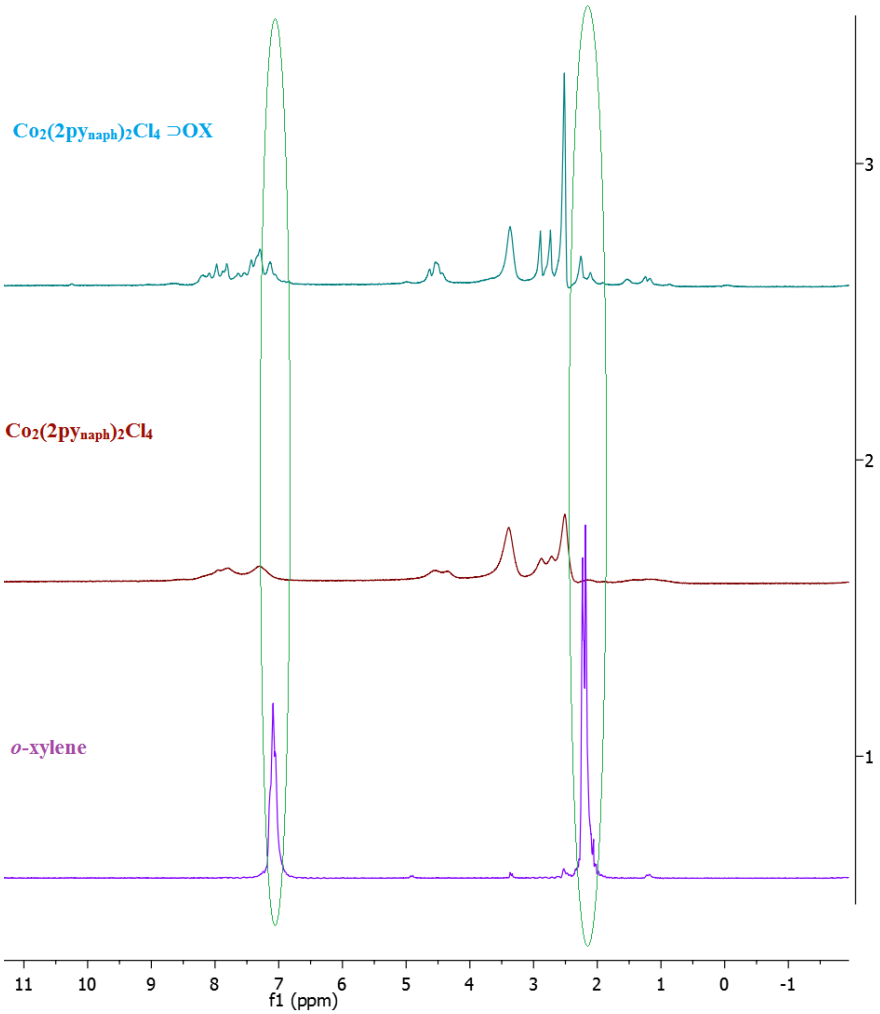

Figure S20 ^{1}H NMR spectra of: *o*-xylene, Co_2(**2py**)$_2Cl_4$, and Co_2(**2py**)$_2Cl_4$⊃OX in DMSO at RT

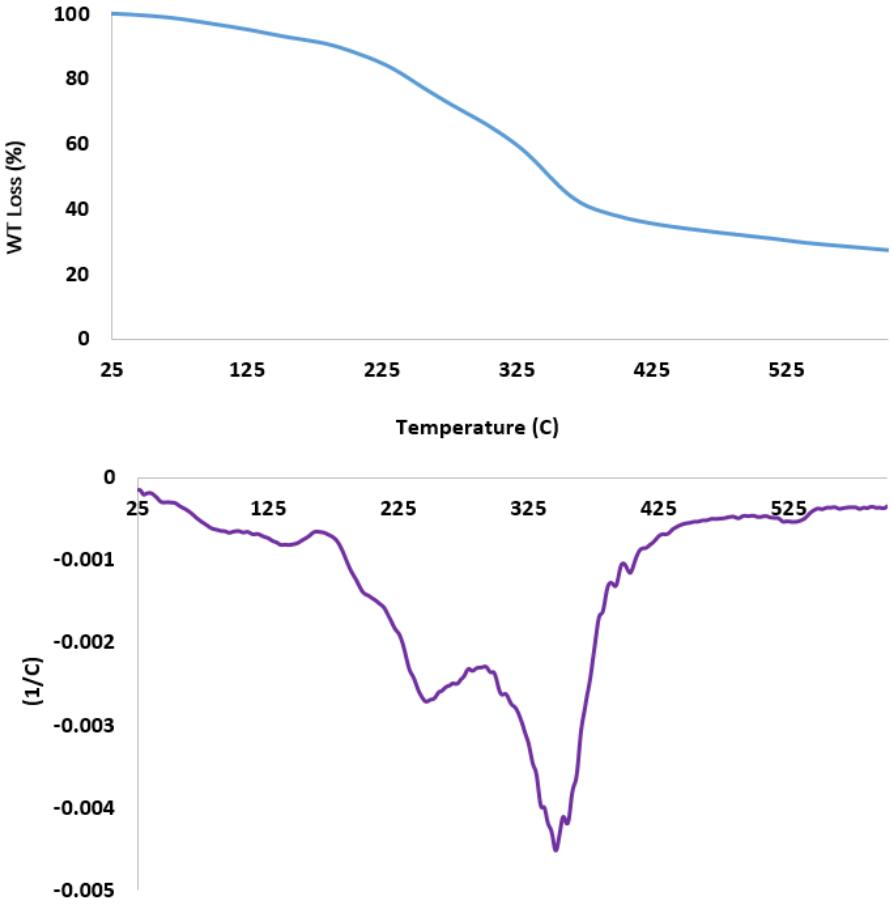

Figure S21 The TGA (top) and DTG (bottom) diagrams of Co_2(**2py**)$_2Cl_4$ ⊃OX

Table S7 The Cartesian coordinates of $Co_2(\mathbf{2py})_2Cl_4$ in DMF

In DMF							
	x	y	z		x	y	z
C	0.27961826	-2.34901138	4.15614857	C	1.80448689	-1.44538529	-9.01977294
C	0.33639413	-1.32549333	6.36570092	C	3.73541633	-1.33393362	-3.7432206
C	-0.51968981	-0.61390362	7.43911236	C	1.63194038	-0.93770312	-2.7104001
C	-1.21451447	-1.38806666	8.38299224	C	0.17463711	-3.94205621	-3.84970497
C	-4.1497702	0.76578811	1.95142709	C	1.7801728	2.69832298	-8.35808652
C	-1.36425254	1.39934811	8.49800671	C	-1.704425	0.36772845	-4.80507554
C	-3.60313491	1.21551963	3.30805995	C	5.09894744	-2.00382664	-1.66794763
C	-1.42225664	0.95809244	2.35520915	C	2.63265897	3.5340841	-9.08930608
C	-0.16336901	3.69770813	2.99149963	C	-0.83666583	-4.4391523	-1.30567716
C	-1.14354872	-2.78252176	8.32349827	C	-1.57311064	-4.83281739	-2.44220549
C	1.88809892	-0.41129861	4.02504713	C	3.51265281	2.98653286	10.02995982
C	-4.93555757	1.61430933	1.17573002	C	-1.06910714	-4.5697915	-3.72736707
C	-1.7960534	-3.56215115	9.28829687	C	0.87217973	0.1634441	-4.81405606
C	0.32928919	5.14751903	0.65971678	C	-1.38662235	1.56472183	-4.17518445
C	1.3334482	5.0362542	1.63829047	C	0.98120477	-0.91169185	-8.01638964
C	-2.53596629	-2.94677362	10.30526511	C	2.65609504	0.76695959	-9.52988314
C	1.08446564	4.31047857	2.81292669	C	3.52648762	1.60179515	10.25022203
C	-0.60294387	-0.16631929	4.48568322	C	-2.23873717	2.05418982	-3.18380551
C	1.62867302	-1.7443034	3.73390818	C	2.4140571	-3.20454912	-2.98544969
C	-0.60663752	0.78109464	7.49719031	C	0.44357246	-3.87851774	-1.45407238
C	-1.96905582	-0.77094912	9.38765724	C	1.53709157	0.40593719	-3.44125231
C	-2.63526967	-1.55001928	10.34672022	C	0.96766068	-3.69627546	-2.73847318
C	2.59929015	-2.48851421	3.05030053	C	0.68904806	-3.16888702	-7.4164149
C	-2.50744585	3.09875587	2.26699129	C	-2.81555338	-0.35012526	-4.39080207
C	-0.91968268	4.54072983	0.86033472	C	2.64282853	-0.61037128	-9.77005154
C	-1.26442454	-0.37901524	3.11294735	C	5.52917709	-1.69440737	-0.36650173
C	-1.15450655	3.79981456	2.0241325	C	0.16143793	-4.04276135	-6.26622053
C	-0.55445855	2.86610888	6.53161019	C	-3.34195094	1.2745689	-2.78388911
C	3.0696358	0.16693786	3.57494032	C	4.15232215	0.19764704	-1.81212378
C	-2.05142879	0.62318063	9.43906684	C	-1.37746776	-4.60955192	-0.02235143
C	-5.28921656	1.21305996	-0.11918041	C	4.6055374	0.4516542	-0.52271089
C	-0.05323803	3.65821337	5.3250965	C	-0.64081609	-4.22679104	1.10683297
C	3.77224698	-1.84628732	2.60003449	C	1.18972555	-3.51828047	-0.3249652
C	-3.8469764	-0.50487553	1.46981651	C	0.64717698	-3.69178402	0.95617304
C	0.5761189	5.86691534	-0.51842742	Cl	5.90187683	1.95184485	2.25754099
C	-4.21712519	-0.84618091	0.16972496	Cl	7.30782699	-1.21436426	2.68026143
C	-0.43148183	6.00648115	-1.47943868	Cl	-5.23843742	-2.52855277	-2.6089764
C	-1.93033906	4.68627828	-0.09837342	Cl	-6.93688756	0.48427672	-3.17858627
C	-1.68663495	5.42068321	-1.26803975	Co	5.57907754	-0.15645805	1.96250499

C	-0.09959933	2.28564815	-4.60045337	Co	-5.14605458	-0.39044689	-2.38206622
C	0.00658934	1.21451699	-6.79506102	H	-0.3374409	-2.44711273	3.28239055
C	0.94730883	0.49607872	-7.81044959	H	0.44850373	-3.30873003	4.59305904
C	1.79702207	1.3153393	-8.57042198	H	1.21724023	-0.7541742	6.16031357
C	4.35476683	-1.05500186	-2.3724042	H	0.61141328	-2.28763232	6.74016365

In DMF

	x	y	z		x	Y	z
H	-1.4198563	2.46652918	8.538783	H	-1.09689313	0.00469775	-5.60164079
H	-4.27935224	1.89620145	3.76971736	H	5.33142106	-2.95180668	-2.10903162
H	-3.47267987	0.35877934	3.93945839	H	2.61116422	4.5918148	-8.92706805
H	-0.4597263	1.40891146	2.23085011	H	-2.51577528	-5.32910199	-2.32534637
H	-1.85343006	0.76064365	1.39562373	H	4.17311612	3.62248202	10.58219118
H	-0.58743585	-3.25233389	7.53948011	H	-1.63365034	-4.8294528	-4.59769345
H	1.18582375	0.1639751	4.58699483	H	-0.08544243	-0.28618658	-4.66621402
H	-5.25650396	2.56353084	1.55793121	H	1.48364314	-0.48427222	-5.404679
H	-1.72980758	-4.6282166	9.24548775	H	4.202379	1.18110807	10.96629468
H	2.28374124	5.50698623	1.48763293	H	-2.0513087	3.00533488	-2.72535085
H	-3.02488542	-3.53950748	11.05089194	H	2.89022366	-3.83720485	-3.70261957
H	1.84142348	4.22138475	3.56346305	H	2.9623611	-3.23115931	-2.06771804
H	0.35346861	0.29142077	4.34486661	H	0.94493668	1.08349622	-2.85938318
H	-1.20888024	0.46432035	5.10210809	H	2.51182878	0.82186292	-3.5840657
H	-3.21808542	-1.07748384	11.11132713	H	0.35098297	-3.54314427	-8.36209493
H	2.4479995	-3.52729265	2.86484912	H	1.75770766	-3.17950186	-7.39376898
H	-3.16146291	3.76425852	2.786681	H	-3.06781648	-1.26781455	-4.88303429
H	-2.93932228	2.83497081	1.32262893	H	3.27459534	-1.02730847	10.52561859
H	-0.6424232	-1.02340948	2.52922026	H	6.0977358	-2.40990813	0.19056244
H	-2.22564405	-0.82707893	3.24826323	H	0.48952842	-5.0572636	-6.36857715
H	-0.3133008	3.38230262	7.43775395	H	-0.90782783	-4.02267404	-6.25092254
H	-1.61779679	2.75638109	6.45918232	H	-3.99629192	1.62288975	-2.006745
H	3.27701692	1.18873632	3.80770624	H	3.64647696	0.95977455	-2.37006399
H	-2.64151319	1.09685769	10.19597213	H	-2.35473662	-5.02868458	0.09410092
H	-5.88503129	1.85309499	-0.73299122	H	4.45457829	1.41780164	-0.08693652
H	-0.48557128	4.63729572	5.32862731	H	-1.05888372	-4.35066545	2.08382478
H	1.01487343	3.74535607	5.35353483	H	2.17293546	-3.11136702	-0.4364625
H	4.51761966	-2.40269832	2.06114512	H	1.21336329	-3.41242725	1.82203989
H	-3.32670136	-1.20804116	2.08642689	N	-0.42680714	-1.48346207	5.11933985
H	1.53609555	6.31168899	-0.6809113	N	-2.30788133	1.87451836	3.08564747
H	-3.96598295	-1.81397149	-0.21950172	N	-4.86945147	0.03380694	-0.60039419
H	-0.24101624	6.55529	-2.37415355	N	3.94551188	-0.53094483	2.84106278
H	-2.88702892	4.23633831	0.06059684	N	0.69080158	1.43699794	-5.50478732
H	-2.46117945	5.53661931	-1.99749468	N	2.37328099	-1.85742244	-3.56020955
H	0.485405	2.4796173	-3.72412523	N	5.21438127	-0.50778716	0.18409602
H	-0.34047487	3.21215684	-5.08210615	N	-3.57021869	0.08502882	-3.37312108

H	-0.87636719	0.63379938	-6.63801275	O	0.06248192	1.58109998	6.5333781
H	-0.25664739	2.16713636	-7.20543677	O	-0.46846858	2.96042826	4.15916545
H	1.79402596	-2.49687714	-9.20797127	O	0.20663949	-1.816791	-7.2235424
H	4.3229724	-2.04364686	-4.28233747	O	0.69136868	-3.47025142	-5.08591985
H	3.68959398	-0.41871591	-4.29183778	H	-1.09689313	0.00469775	-5.60164079
H	0.64874056	-1.32344733	-2.54219097	H	5.33142106	-2.95180668	-2.10903162
H	2.12911573	-0.81588678	-1.77151932	H	2.61116422	4.5918148	-8.92706805
H	1.11423217	3.11572096	-7.63397637	H	-2.51577528	-5.32910199	-2.32534637

Table S8. Relative energy of existing van der Waals interactions in crystal structure of Co_2(**2py**)$_2Cl_4$

Name	Interaction Type	Distance (Å)	Relative Energy (kcal mol^{-1})
Co_2(**2py**)$_2Cl_4$	π-π Interaction	4.349	2.593
	H-π Interaction	2.748	6.361
	H-π Interaction	2.968	4.932

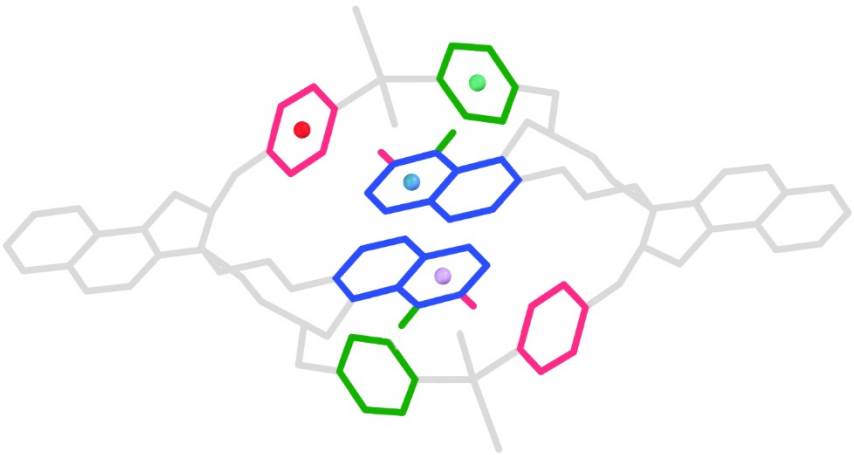

Figure S22 Schematic representation of existing van Der Waals interactions in the crystal structure of Co_2(**2py**)$_2Cl_4$, π-π interaction (blue), H-π interaction-face (green), and H-π interaction-side (pink). Hydrogens were removed for clarity

Table S9 Relative energies of different conformations relative to the crystal structure of Co_2(**2py**)$_2Cl_4$

Conformation	Relative energy (kcal mol^{-1})
1	0
2	24.066
3	24.268
4	24.504
5	24.581
Crystal structure	0
in DMF	14.798

Table S10 Some selected bond lengths [Å], distances [Å], and angles [°] for Co_2(**2py**)$_2Cl_4$

Parameter	Distance		Parameter	Angle	
	Solid	Solution		Solid	Solution
Co … Co	12.127	13.574	py_1-Co- py_2	104.08	103.81
naph … naph	4.348	7.778	py_3-Co- py_4	104.08	108.48
py_1 … py_3	9.383	8.771	naph … naph	0.5	13.04
py_2 … py_4	8.022	8.113			

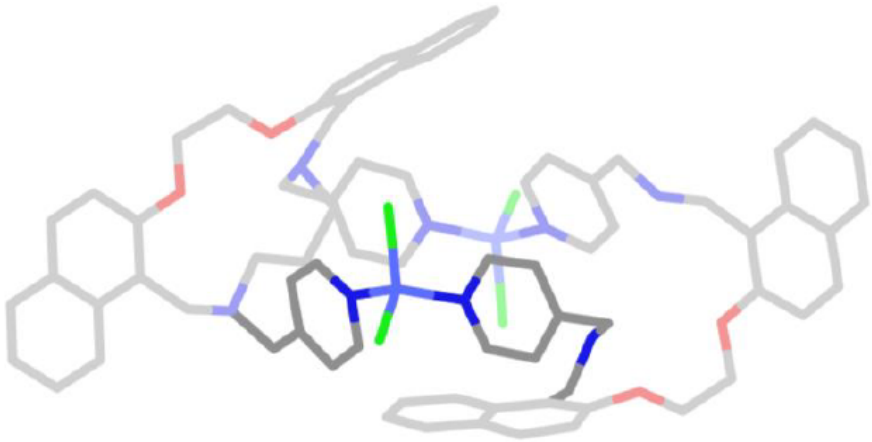

Figure S23 Molecular view of the optimized ground state geometry of Co_2(**2py**)$_2Cl_4$ in DMF

Table S11 Relative energy of different conformations relative to the optimized structure

Conformation	Relative energy (kcal mol^{-1})
optimized structure	0
o-xylene	12.451
m-xylene	18.533
p-xylene	N.A.

Table S12 The orbital contribution excitation of Co_2(**2py**)$_2Cl_4$ in gas state

From	To	Contribution	
SHOMO	LUMO	0.388318	39.0%
SHOMO-1	LUMO+1	0.402401	40.2%

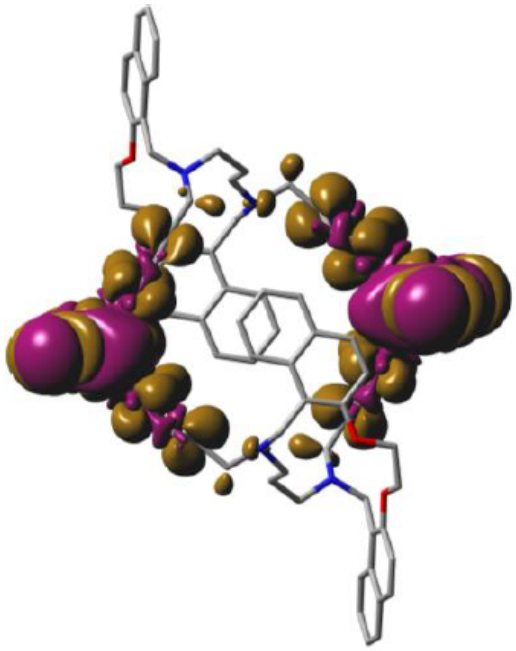

Figure S24 PBE0-DFT transition densities for Co_2(**2py**)$_2Cl_4$. During the electronic transition, the electron density increases the violet areas and decreases in the brown areas

Table S13 Comparison of the computational and experimental optical data

Co_2(**2py**)$_2Cl_4$	Excitation (λ_{ex})		Emission (λ_{em})	
	theor	exp	theor	exp
	332	340	439	456