Supplementary Information

Selective and Reversible Adsorption of Cationic Dyes by Mixed Ligand Zn(II) Coordination Polymers Synthesized by Reactants Ratio Modulation

Yadagiri Rachuri,[a,b] Sreevalsa Subhagan,[b] Bhavesh Parmar,[a,b] Kamal Kumar Bisht[c] and Eringathodi Suresh[a,b]*

[a]Academy of Scientific and Innovative Research (AcSIR), CSIR–Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364 002, Gujarat, India.

[b]Analytical and Environmental Science Division & Centralized Instrument Facility, CSIR–Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364 002, Gujarat, India.

[c]Department of Chemistry, RCU Government Post Graduate College, Uttarkashi-249193, Uttarakhand, India.

E-mail: esuresh@csmcri.res.in; sureshe123@rediffmail.com

Synthesis of 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L):

Ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene **(**L**)** was synthesized by adopting the procedure reported by Bisht *et.al* with slight modifications.[1] Pyridine-4-carboxaldehyde (4 mL, 40 mmol) and hydrazine hydrate (1 mL, 21 mmol) were separately dissolved in 7.5 mL of ethanol each. The resulting solutions were mixed gently and allowed to stir at room temperature for 20 min. The yellow precipitate thus obtained was collected and washed with cold methanol/ether mixture (1:1, 10 mL) and dried in air. Yield = 92%. 1H NMR (DMSO-*d6*): δ7.82(d,4H), 8.70(s,2H), 8.76(d,4H).

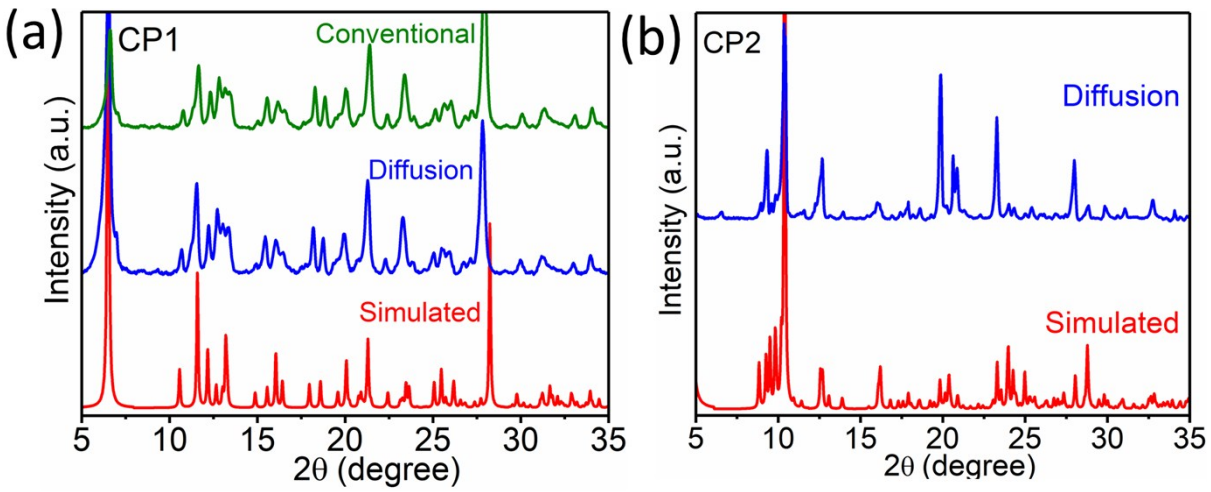

Figure S1. Experimental PXRD profiles of bulk samples for **CP1** and **CP2** (diffusion and conventional) were confirmed by simulated patterns.

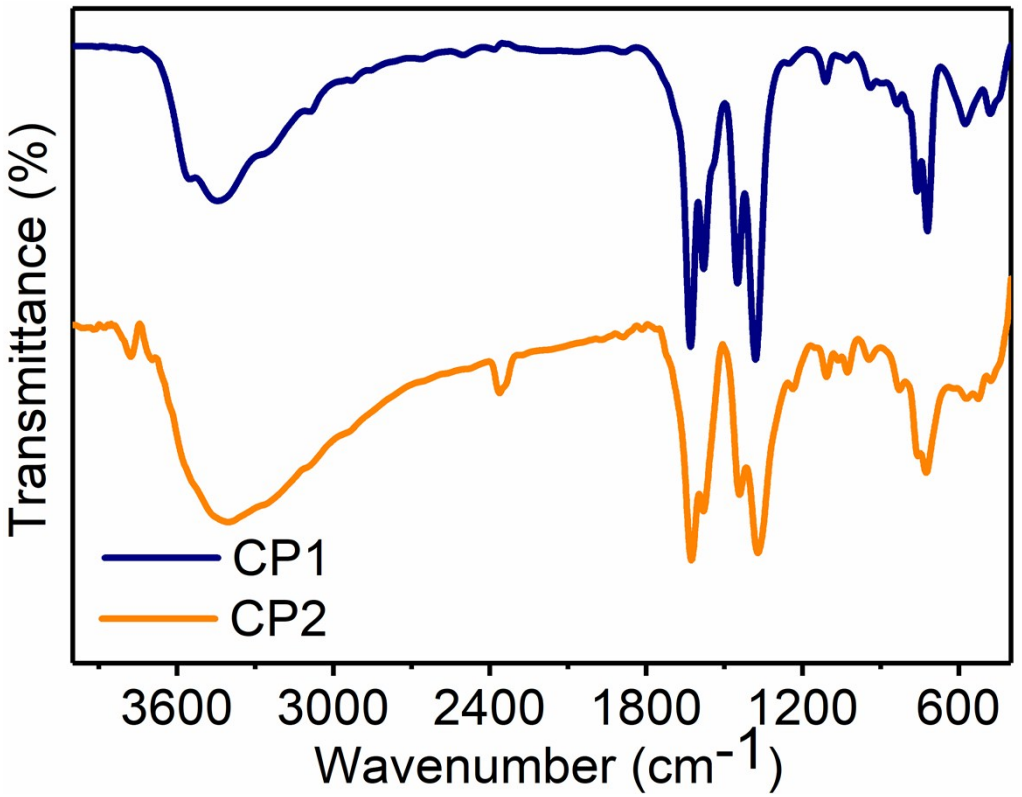

Figure S2. IR spectra recorded for compound **CP1** and **CP2** dispersed in KBr pellets in N_2 atmosphere.

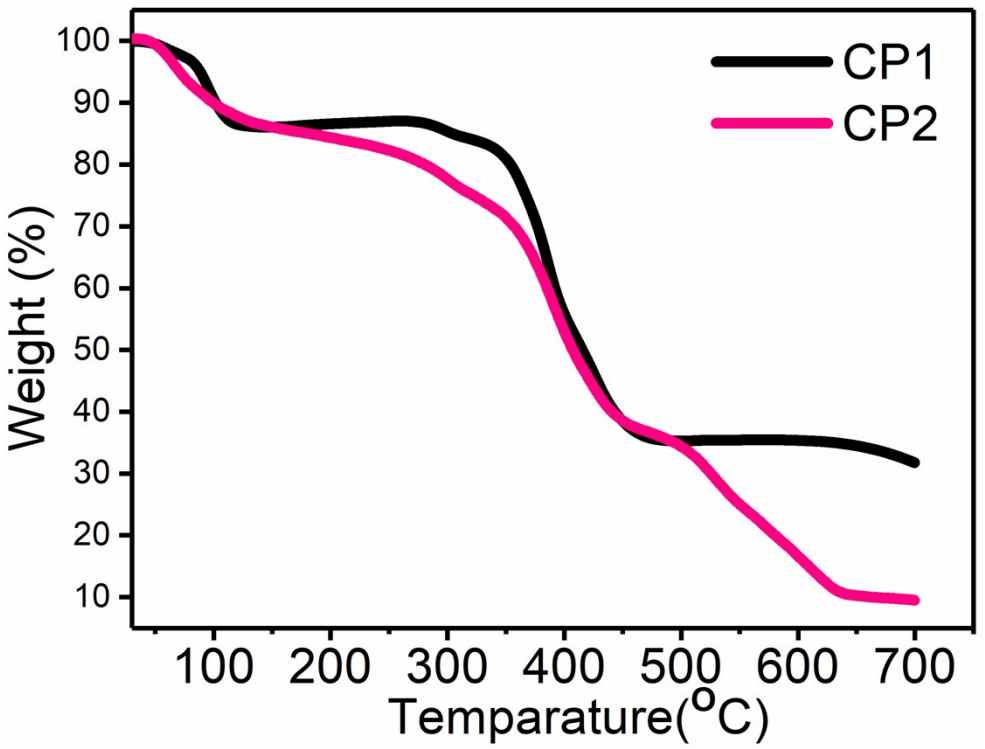

Figure S3. TGA profiles recorded for compound **CP1** and **CP2** in N_2 atmosphere.

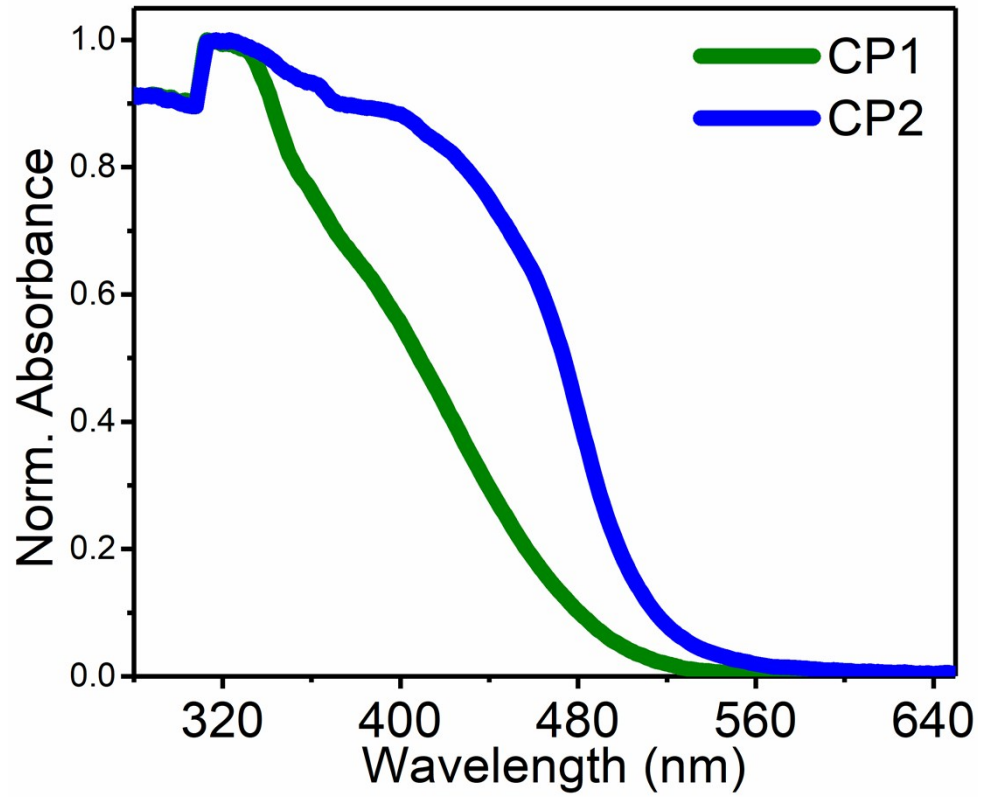

Figure S4. Solid state UV-Vis absorbance spectra for pristine samples of **CP1** and **CP2**.

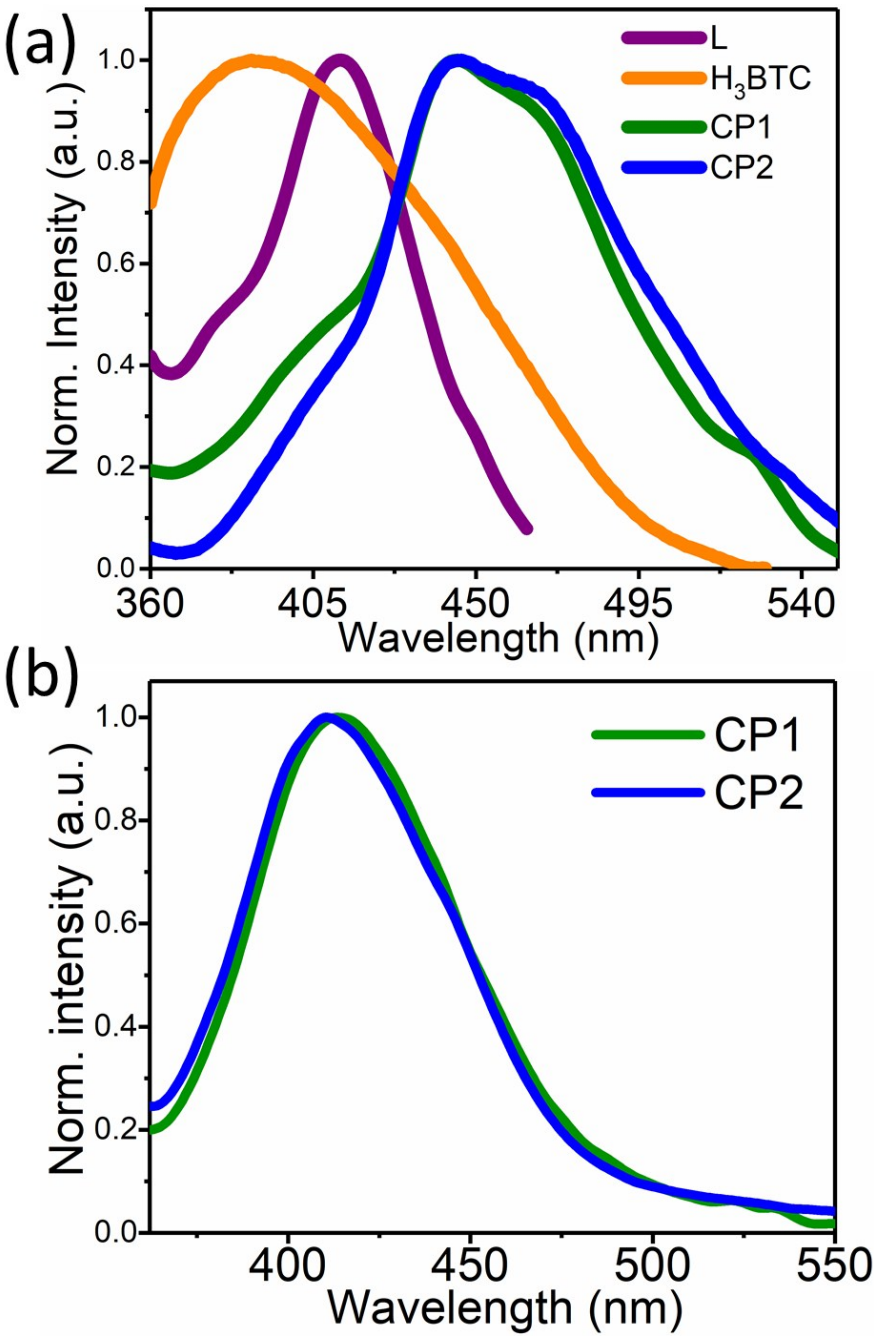

Figure S5. (a & b) Photoluminescence spectra of L, H_3BTC, **CP1** and **CP2** in the solid state and the suspension of DMF.

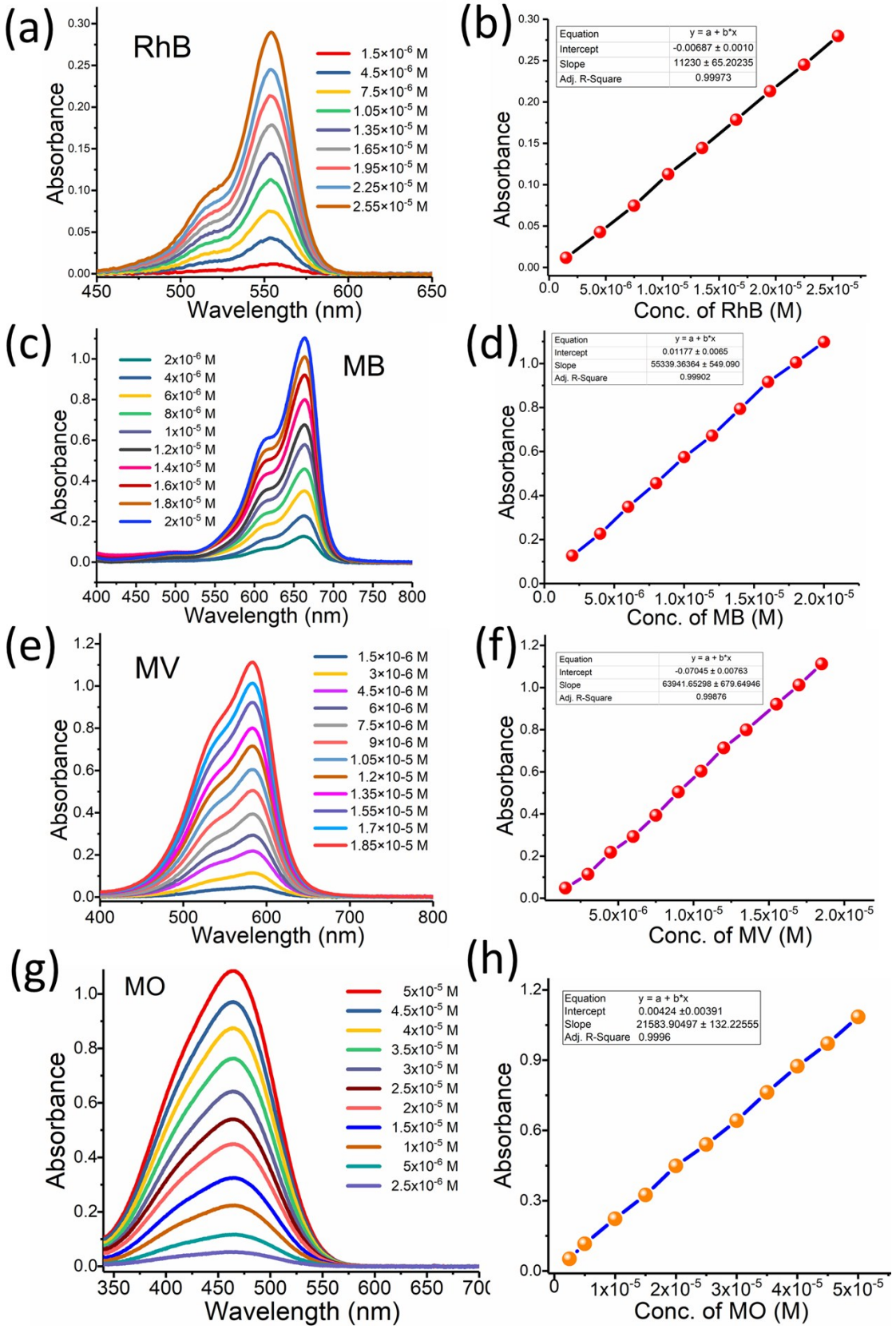

Figure S6. Calibration plots of standard RhB, MB, MV and MO (a, c, e & g) by UV-Vis spectra in an aqueous solution and their fitting of Abs. vs concentration of respective dye values (b, d, f & h).

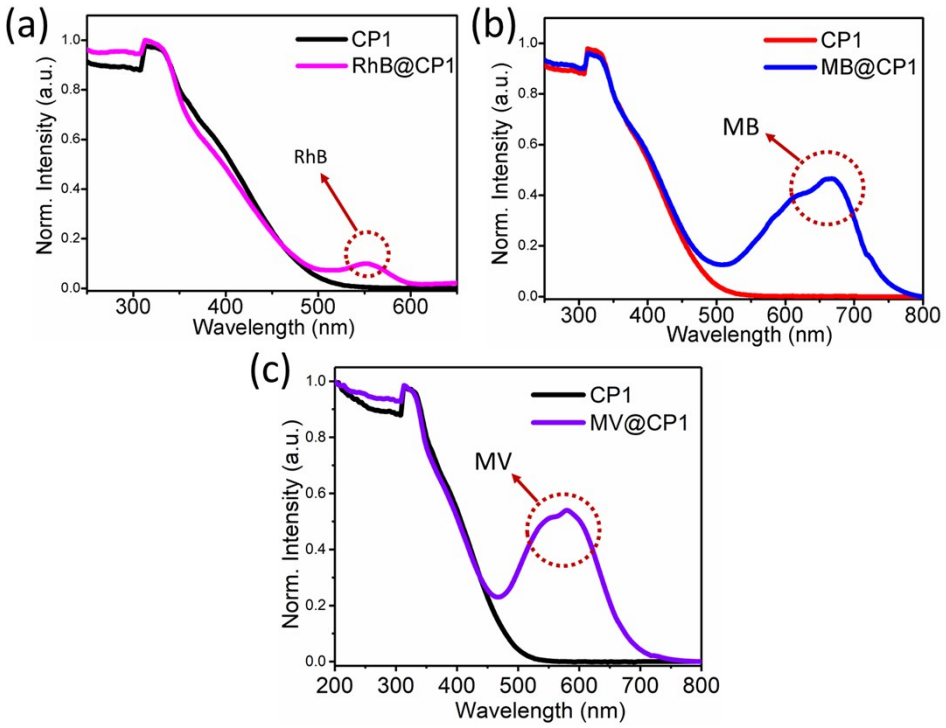

Figure S7. Solid state UV-Vis spectra of **CP1@Dye** materials confirming the adsorbates characteristic bands at particular wavelengths after adsorption of dyes.

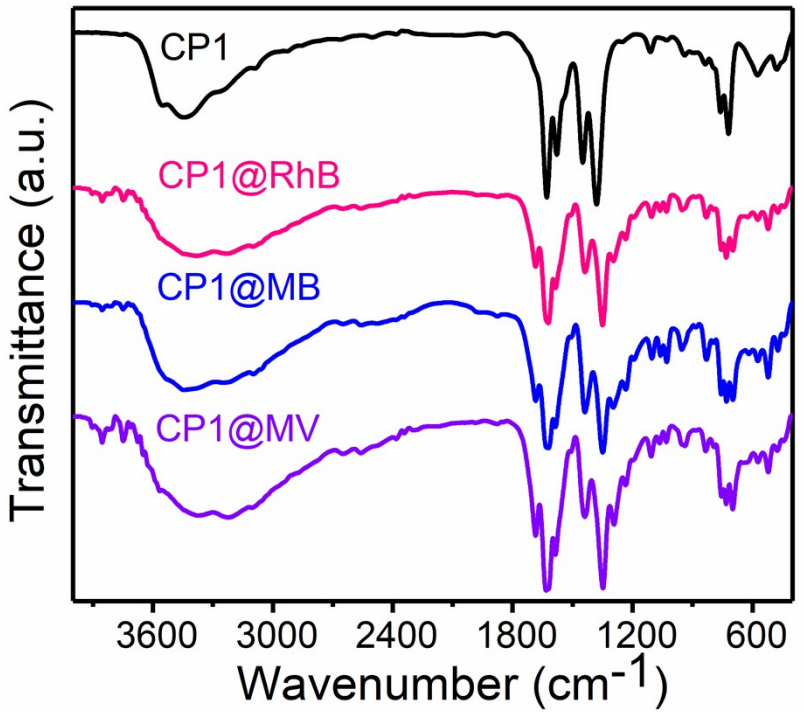

Figure S8. FTIR spectra of **CP1@dye** confirming the framework integrity of **CP1** before and after adsorption of cationic dyes.

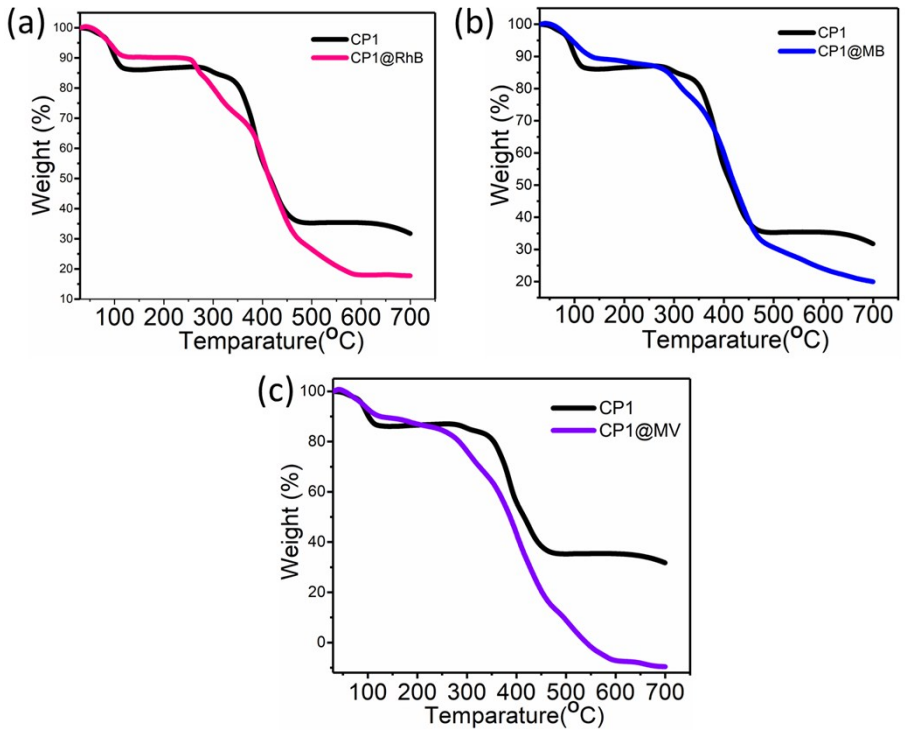

Figure S9. TGA profiles of **CP1@Dye** recorded in N_2 atmosphere confirming thermal stability before and after adsorption dyes.

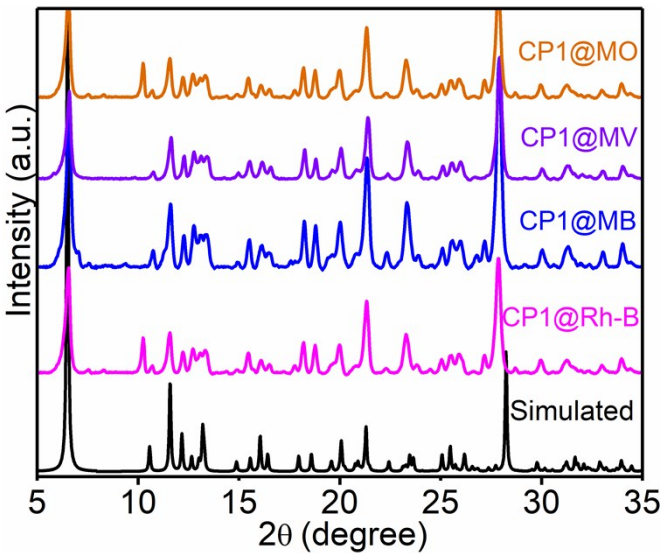

Figure S10. PXRD patterns of **CP1@Dye** confirming the framework stability after adsorption of dye from aqueous solutions.

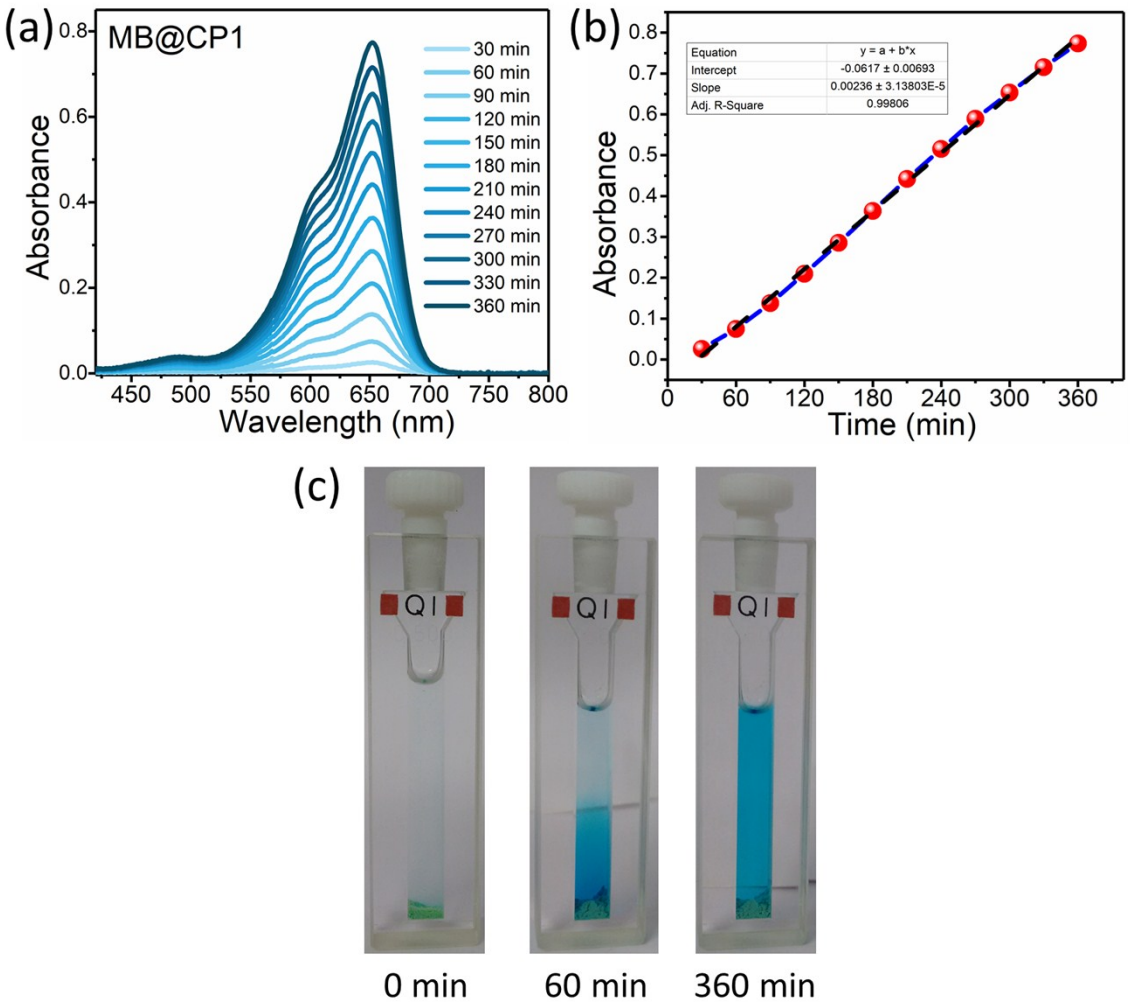

Figure S11. Time dependent UV-Vis spectra depicting enhancement in the absorbance (λ_{max} 652 nm) suggesting increase in MB concentration with time (a), absorbance-time profile showing linear release of MB (30 to 360 min) (b) and digital photographs showing progressive color change due to release of adsorbed MB in 0.5 mL MeOH after soaking 10 mg of **CP1@MB** (c).

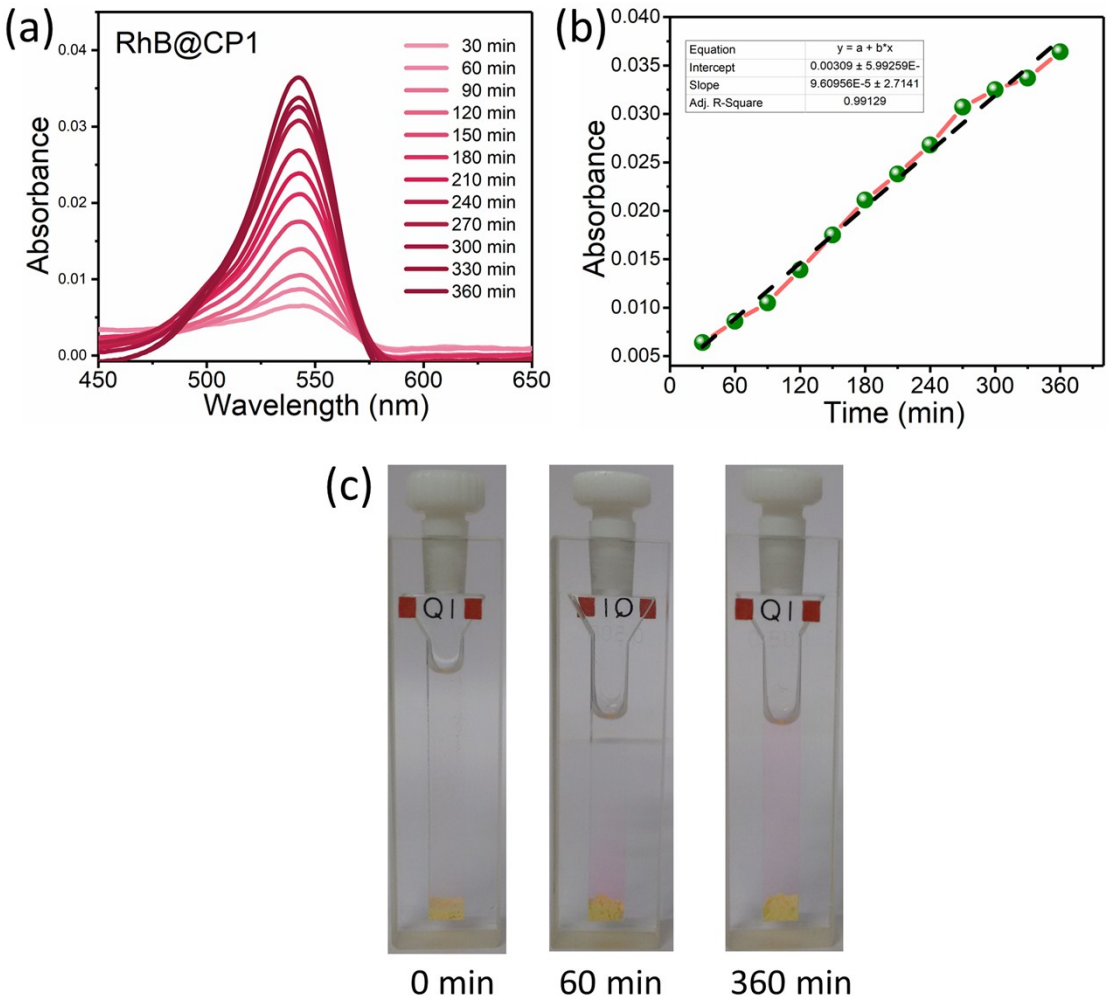

Figure S12. Time dependent UV-Vis spectra depicting enhancement in the absorbance (λ_{max} 542 nm) suggesting increase in RhB concentration with time (a), absorbance-time profile showing linear release of RhB (30 to 360 min) (b) and digital photographs showing progressive color change due to release of adsorbed RhB in 0.5 mL MeOH after soaking 10 mg of **CP1@RhB** (c).

Table S1. Details of hydrogen bonding interactions observed in the structure of **CP2**.

D-H···A	d(H···A) (Å)	d(D···A) (Å)	∠D-H···A (°)
CP2			
O7-H7B···O1AA#1	2.04	2.914	172.5
O10-H10A···N6#1	1.84	2.697	168.6
O11-H11A···O0AA#1	2.17	2.900	141.0
O11-H11B···O9	1.78	2.585	152.9
O7-H7A···O7#3	2.21	3.060	162.9
O7-H7A···O7#2	2.21	3.060	162.9
Symmetry code: #1. x, y, z, #2. -1+x, +y, +z, #3. 1-x, 1-y, 2-z.			

Table S2. Zeta potential values of **CP1** and **CP1@dye** materials.

Composition	Zeta Potential (mV)
CP1	-21
CP1@MO	-22
CP1@RhB	-18.4
CP1@MB	-17.4
CP1@MV	-11.5

Table S3. Crystal Data and Refinement Parameters for **CP1** and **CP2**.

Identification code	**CP1**	**CP2**
Chemical formula	$C_{36}H_{40}N_4O_{17}Zn_2$	$C_{65}H_{96}N_{12}O_{33}Zn_5$
Formula weight	931.46	1900.38
Crystal Colour	Pale Yellow	Pale Yellow
Crystal Size (mm)	0.28 × 0.25 × 0.03	0.20 × 0.11 × 0.04
Temperature (K)	150(2)	150(2)
Crystal System	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.9461(12)	10.3241(17)
b (Å)	9.0703(13)	11.0585(18)
c (Å)	14.198(2)	19.221(3)
α(°)	77.108(2)	85.079(3)
β(°)	75.211(2)	83.258(3)
γ (°)	68.670(2)	64.713(3)
Z	1	1
V (Å^3)	911.9(2)	1968.9(6)
Density (Mg/m^3)	1.696	1.603
Absorption Coefficient (mm^{-1})	1.403	1.596
F(000)	480	984
Reflections Collected	6481	14187
Independent Reflections	3170	6892
$R_{(int)}$	0.0174	0.0579
Number of parameters	292	450
S(Goodness of Fit) on F^2	1.071	1.123
Final R1/wR2 (I>2σ(I))	0.0289/0.0778	0.0877/0.1998
Weighted R1/wR2 (all data)	0.0298/0.0784	0.1104/0.2101
CCDC Numbers	1560856	1560857
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$; $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$		

Table S4. Selected bond lengths and bond angles for **CP1** and **CP2**.

CP1			
Zn(1)-O(1)	1.9493(14)	O(5)#1-Zn(1)-N(1)	129.17(7)
Zn(1)-O(5)#1	1.9508(14)	O(1)-Zn(1)-O(7)	97.95(6)
Zn(1)-N(1)	2.0316(18)	O(5)#1-Zn(1)-O(7)	97.98(6)
Zn(1)-O(7)	2.0777(15)	O(5)- Zn1-O(7)	175.18(6)
O(1)-C(7)	1.277(3)	N(1)-Zn(1)-O(7)	95.89(7)
O(2)-C(7)	1.239(3)	C(7)-O(1)-Zn(1)	119.81(13)
O(3)-C(8)	1.271(3)	C(9)-O(5)-Zn(1)#2	116.46(13)
O(4)-C(8)	1.262(3)	C(10)-N(1)-Zn(1)	118.24(15)
O(5)-C(9)	1.290(3)	C(14)-N(1)-Zn(1)	123.57(15)
O(5)-Zn(1)#2	1.951(2)	C(15)-N(2)-N(2)#3	111.3(3)
N(2)-N(2)#3	1.411(4)	O(2)-C(7)-O(1)	125.20(19)
O(1)-Zn(1)-O(5)#1	123.84(6)	O(4)-C(8)-O(3)	124.0(2)
O(1)-Zn(1)-N(1)	102.03(7)	O(6)-C(9)-O(5)	123.57(19)
Symmetry code: #1. x-1, y+1, z; #2. x+1, y-1, z; #3. -x-1, -y+1, -z+2.			
CP2			
Zn(3)-O(8)	2.062(5)	O(9)#4-Zn(3)-Zn(2)#4	46.13(18)
Zn(3)-O(8)#4	2.062(5)	O(9)-Zn(3)-Zn(2)#4	133.87(18)
Zn(3)-O(3)#2	2.075(5)	O(8)-Zn(1)-O(1)	114.9(3)
Zn(3)-O(3)#3	2.075(5)	O(8)-Zn(1)-O(6)#1	131.3(3)
Zn(3)-O(9)#4	2.138(5)	O(1)-Zn(1)-O(6)#1	107.4(3)
Zn(3)-O(9)	2.138(5)	O(8)-Zn(1)-N(1)	102.9(3)
Zn(1)-O(8)	1.970(5)	O(1)-Zn(1)-N(1)	95.7(3)
Zn(1)-O(1)	1.986(5)	O(6)#1-Zn(1)-N(1)	95.6(3)
Zn(1)-O(6)#1	1.997(5)	O(2)-Zn(2)-O(4)#2	169.7(3)
Zn(1)-N(1)	2.133(7)	O(2)-Zn(2)-N(3)	95.1(3)
Zn(2)-O(2)	2.027(5)	O(4)#2-Zn(2)-N(3)	94.0(3)
Zn(2)-O(4)#2	2.027(5)	O(2)-Zn(2)-O(8)	92.0(3)
Zn(2)-N(3)	2.102(7)	O(4)#2-Zn(2)-O(8)	92.3(2)
Zn(2)-O(8)	2.099(5)	N(3)-Zn(2)-O(8)	93.1(3)
Zn(2)-O(7)	2.118(5)	O(2)-Zn(2)-O(7)	85.2(3)

Zn(2)-O(9)	2.242(5)	N(3)-Zn(2)-O(7)	96.8(3)
O(3)-Zn(3)#5	2.075(5)	O(8)-Zn(2)-O(7)	169.7(2)
O(4)-Zn(2)#5	2.027(5)	O(2)-Zn(2)-O(9)	83.9(2)
O(6)-Zn(1)#6	1.997(5)	O(4)#2-Zn(2)-O(9)	87.5(2)
N(2)-N(2)#7	1.426(16)	N(3)-Zn(2)-O(9)	173.2(2)
N(4)-N(5)	1.443(12)	O(8)-Zn(2)-O(9)	80.03(19)
O(8)-Zn(3)-O(8)#1	180.0	O(7)-Zn(2)-O(9)	89.8(2)
O(8)-Zn(3)-O(3)#3	83.4(2)	N(1)–Zn(1)–O(3)	171.54(5).
O(8)#4-Zn(3)-O(3)#2	83.4(2)	C(1)-O(1)-Zn(1)	119.5(5)
O(8)-Zn(3)-O(3)#3	83.4(2)	C(1)-O(2)-Zn(2)	151.3(5)
O(8)#4-Zn(3)-O(3)#3	96.6(2)	C(8)-O(3)-Zn(3)#5	124.2(5)
O(3)#3-Zn(3)-O(3)#2	180.0(3)	C(8)-O(4)-Zn(2)#5	133.7(5)
O(8)-Zn(3)-O(9)#4	96.6(2)	C(9)-O(6)-Zn(1)#6	110.0(5)
O(8)#4-Zn(3)-O(9)#4	83.4(2)	Zn(1)-O(8)-Zn(3)	111.0(2)
O(3)#3-Zn(3)-O(9)#4	91.9(2)	Zn(1)-O(8)-Zn(2)	115.4(2)
O(3)#3-Zn(3)-O(9)#4	91.9(2)	Zn(3)-O(8)-Zn(2)	96.8(2)
O(8)-Zn(3)-O(9)	83.4(2)	Zn(3)-O(9)-Zn(2)	90.6(2)
O(8)#4-Zn(3)-O(9)	96.3(2)	C(14)-N(1)-Zn(1)	120.2(6)
O(3)#2-Zn(3)-O(9)	88.1(2)	C(10)-N(1)-Zn(1)	121.4(6)
O(3)#3-Zn(3)-O(9)	88.1(2)	C(20)-N(3)-Zn(2)	121.0(6)
O(9)#4-Zn(3)-O(9)	180.0(3)	C(16)-N(3)-Zn(2)	117.0(8)
O(8)-Zn(3)-Zn(2)#4	137.97(14)	O(1)-C(1)-O(2)	124.4(7)
O(8)#4-Zn(3)-Zn(2)#4	42.03(14)	O(4)-C(8)-O(3)	126.5(7)
O(3)#3-Zn(3)-Zn(2)#4	80.17(14)	O(5)-C(9)-O(6)	122.1(7)
O(4)#2-Zn(2)-O(7)	88.9(2)		
Symmetry code: #1.-1+X,+Y,+Z; #2.+X,-1+Y,+Z; #3.1-X,2-Y,2-Z; #4.1-X,1-Y,2-Z; #5.+X,1+Y,+Z; #6.1+X,+Y,+Z; #7.1-X,2-Y,1-Z			

References

1. K. K. Bisht, P. Patel, Y. Rachuri and E. Suresh, *Acta Crystallogr. Sect. B*, 2014, **B70**, 63.