

Electronic Supplementary Information

The preparation of new Covalent Organic Framework (COF) embedded with silver nanoparticles and its applications in degradation of organic pollutants from waste water

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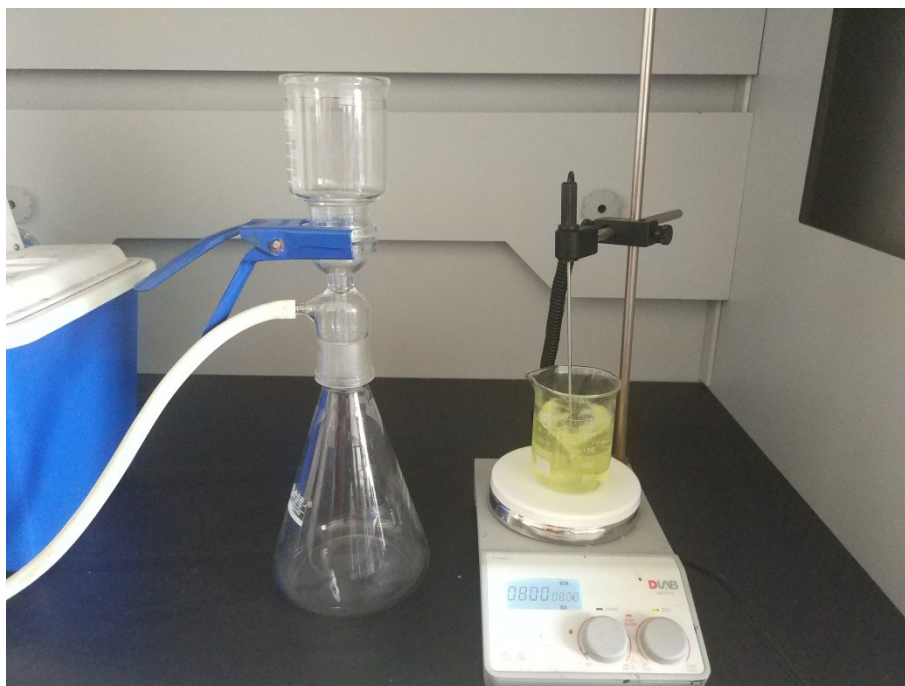


Fig. S1 Digital photograph of the experimental device for the reduction of 4-NP polluted water.

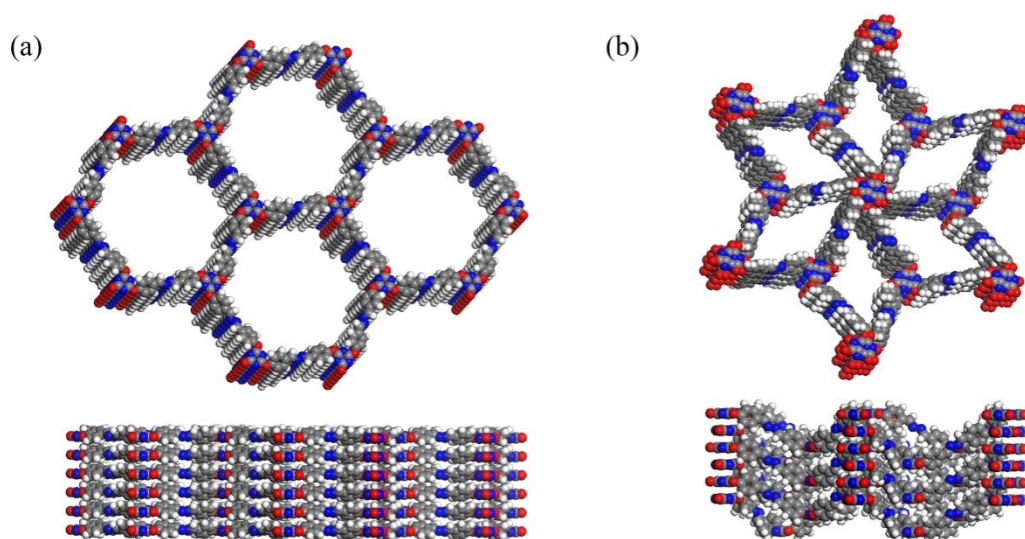


Fig. S2 (a) AA stacking mode of TPHH-COF (top and side view); (b) AB stacking mode of TPHH-COF (top and side view).

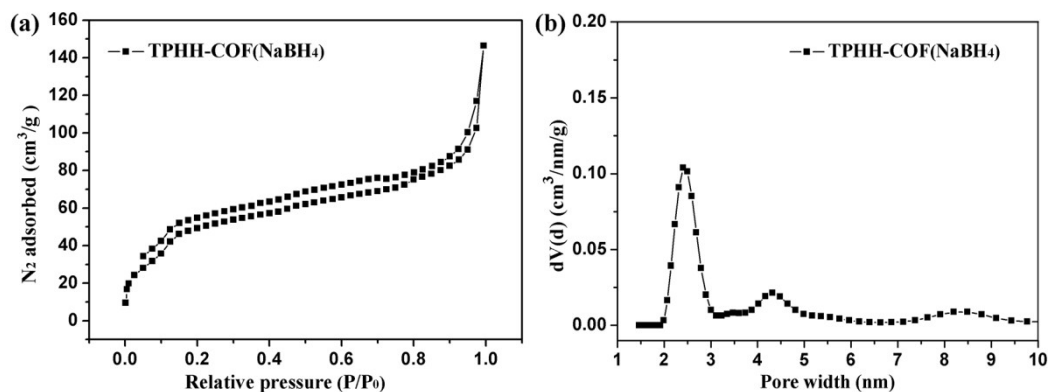


Fig. S3 (a) N₂ adsorption isotherms of TPHH-COF treated with NaBH₄; (b) The pore widths of TPHH-COF NaBH₄ centered at 2.4 nm.

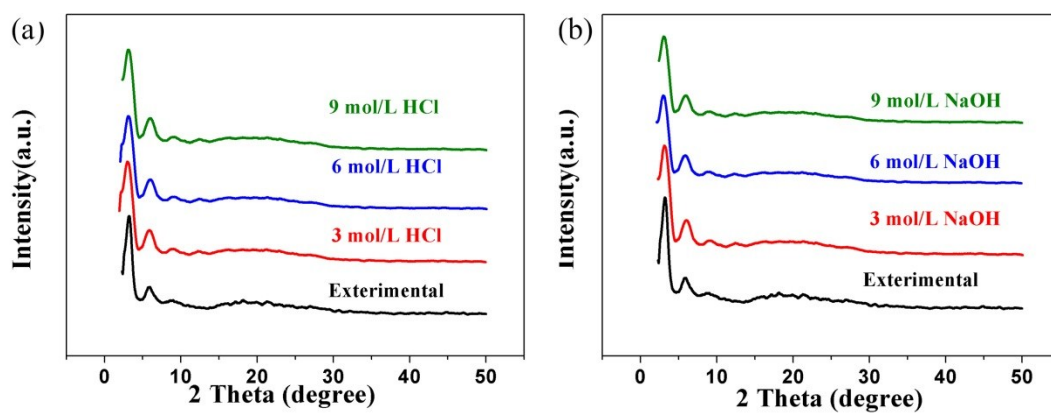


Fig. S4 The PXRD patterns of TPHH-COF in different conditions: a series of HCl solutions (3 mol/L, 6 mol/L, 9 mol/L) and NaOH solutions (3 mol/L, 6 mol/L, 9 mol/L).

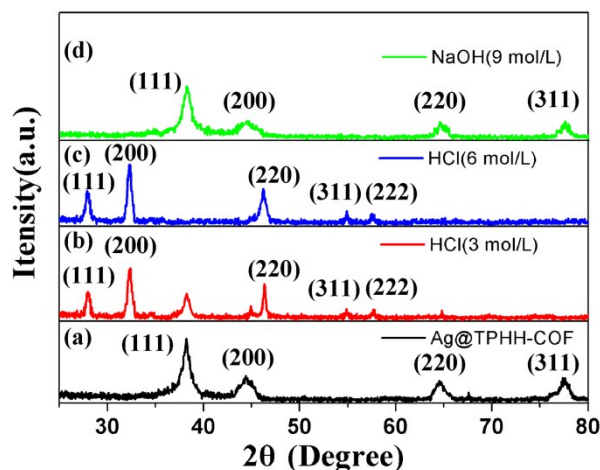


Fig. S5 The PXRD patterns of Ag@TPHH-COF in different conditions (2θ range: 25° - 80°) (a) Ag@TPHH-COF without any treatment. (b) Ag@TPHH-COF was immersed in HCl (aq., 3 mol/L) for 24 hours. (c) Ag@TPHH-COF was immersed in HCl (aq., 6 mol/L) for 24 hours. (d) Ag@TPHH-COF was immersed in NaOH (aq., 9 mol/L) for 24 h.

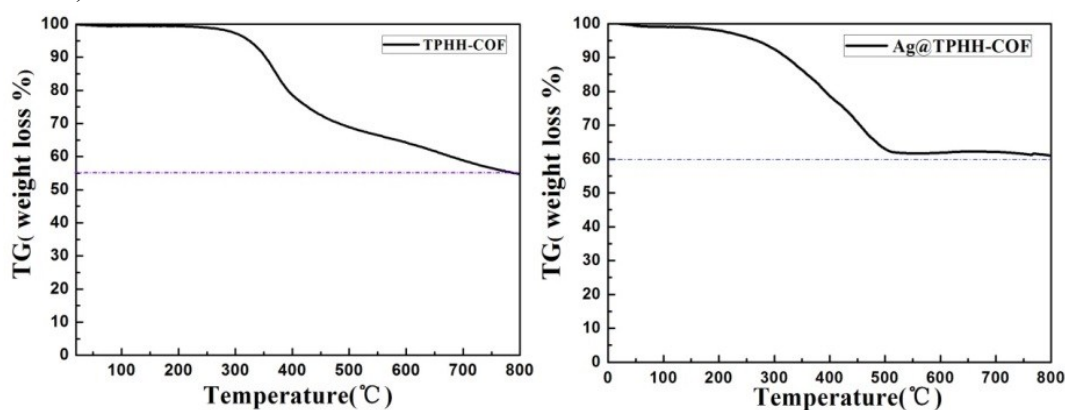


Fig. S6 TGA graphs of TPHH-COF and Ag@TPHH-COF.

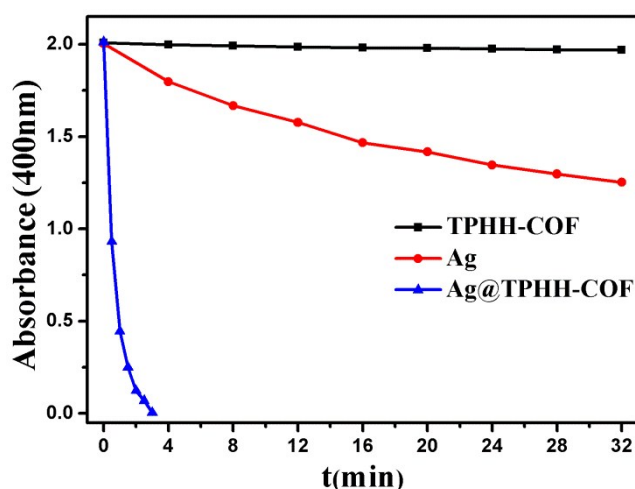


Fig. S7 The time-dependent UV-vis absorption spectra of 4-NP solution (400 nm) in the presence of NaBH_4 and TPHH-COF (4 mg), Ag (4 mg), Ag@TPHH-COF (4 mg) was used as catalyst, respectively.

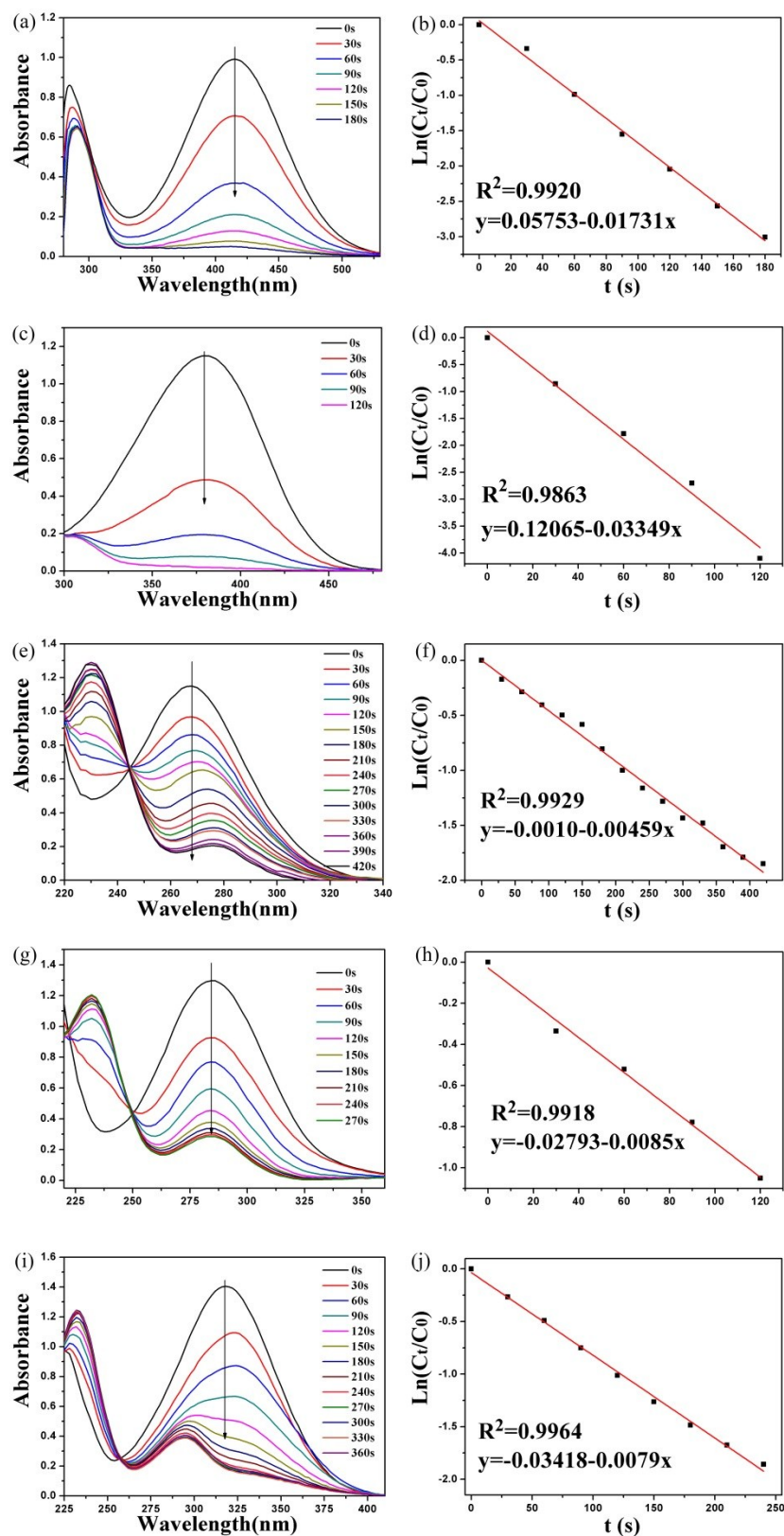


Fig. S8 The UV-vis absorption spectra (left) and the plot of $\ln(C_t/C_0)$ versus reaction time (right) for the reduction of NACs: (a, b) 2-nitrophenol, (c, d) 4-nitroaniline, (e, f) nitrobenzene, (g, h) 4-nitrotoluene, (i, j) 1-butyl-4-nitrobenzene.

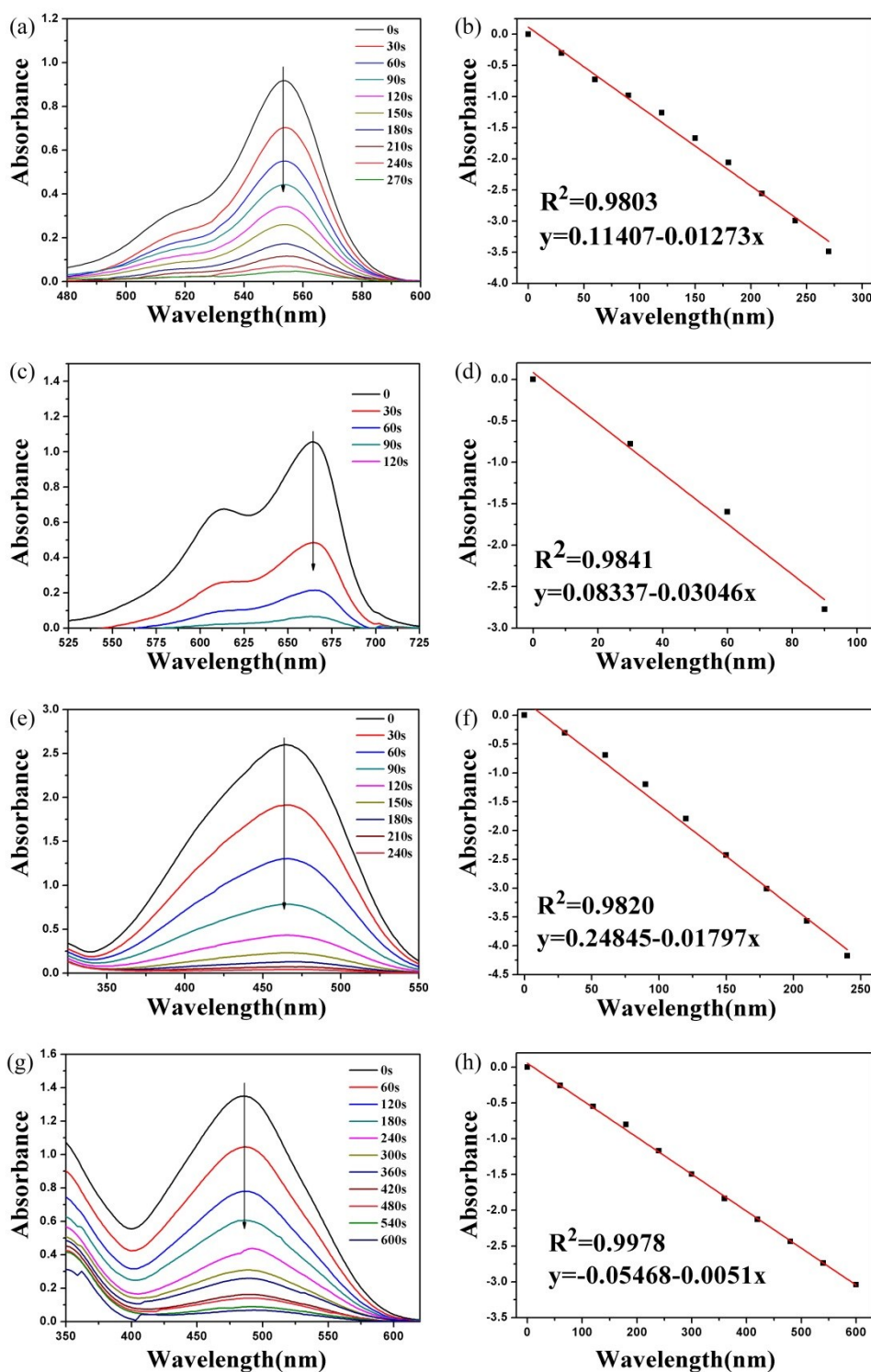


Fig. S9 The UV-vis absorption spectra (left) and the plots of $\ln(C_t/C_0)$ versus reaction time (right) for the reduction of dyes: (a, b) [RhB] = 1×10^{-5} mol/L, (c, d) [MB] = 2×10^{-5} mol/L, (e, f) [MO] = 5×10^{-5} mol/L, (g, h) [CR] = 1×10^{-4} mol/L.

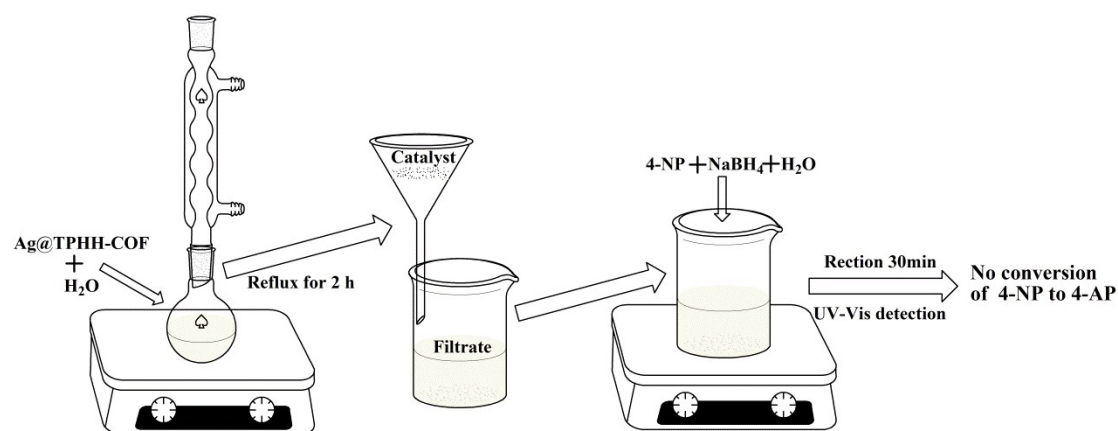


Fig. S10 Typical catalyst leaching test performed for Ag@TPHH-COF catalyst: 50 mg of Ag@TPHH-COF catalyst and 4 ml H_2O was added into a round bottom flask. This catalyst was refluxed for 2 h and filtered in hot conditions into conical flask. To this catalyst free, filtrate solution required amount of the substrates (4-NP and NaBH_4) was added and stirred at room temperature and reaction progress was traced using UV-Vis spectroscopy. The absence of the any trace of product after 30 min reaction confirmed the heterogeneous behavior of the catalyst.

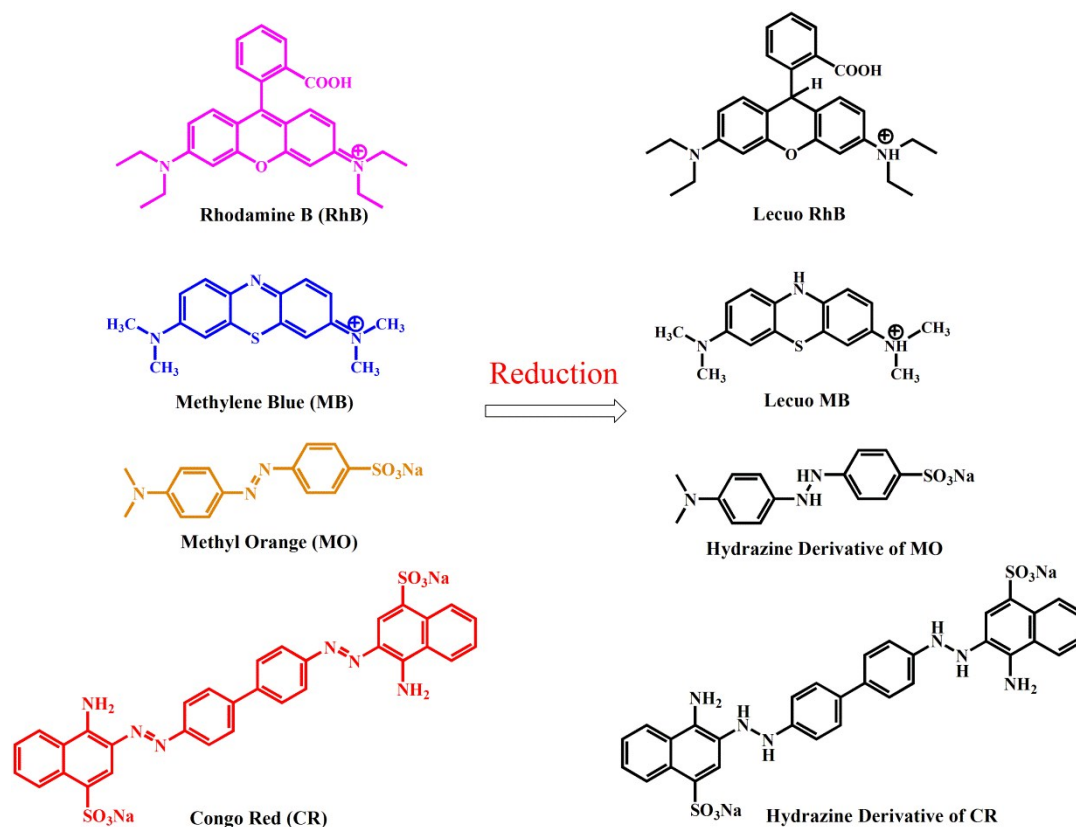


Fig. S11 Reduction reactions of dyes to their leuco forms (hydrazine derivative for MO and CR).

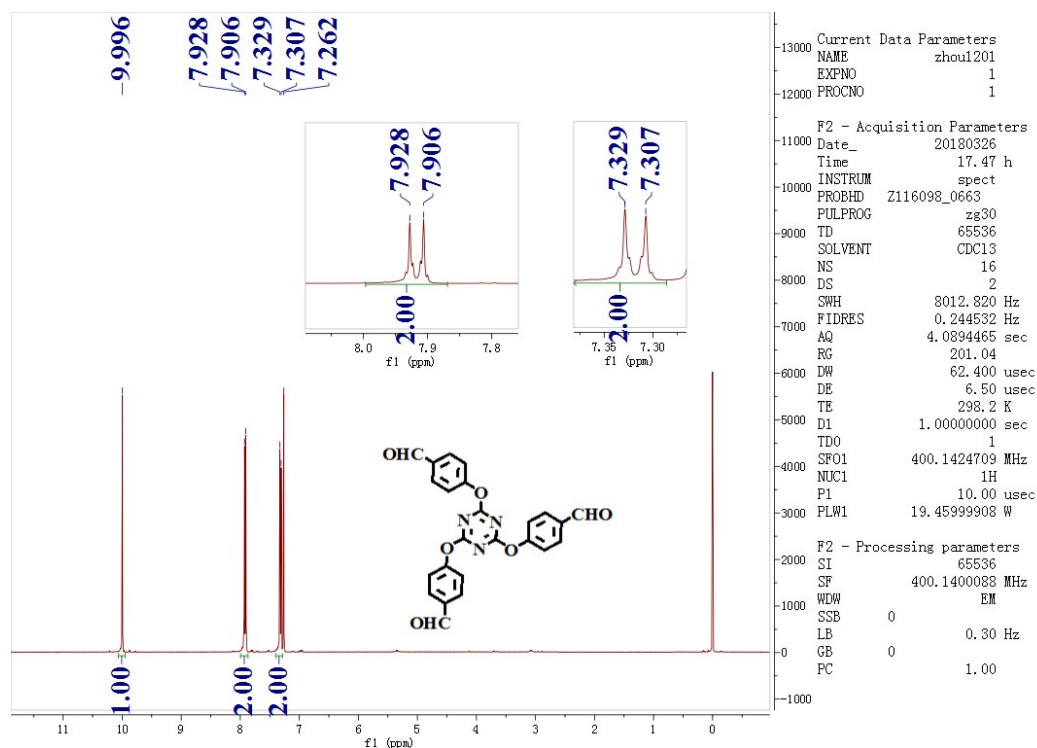


Fig. S12 ^1H NMR spectrum of TPT-CHO.

Table S1 Fractional atomic coordinates for the unit cell of TPHH-COF calculated based on eclipsed AA model.

Space group	P6		
Unit cell	$a = b = 31.642 \text{ \AA}, c = 3.8967 \text{ \AA}, \alpha = \beta = 90^\circ, \gamma = 120^\circ$		
Pawley refinement	$R_p = 2.91\%, R_{wp} = 3.76\%$		
atom	x	y	z
C1	0.78982	0.36025	0.04016
C2	0.82807	0.3561	-0.10527
C3	0.8761	0.39301	-0.07073
C4	0.88819	0.43586	0.11166
C5	0.84967	0.43919	0.26062
C6	0.80154	0.4022	0.23145
C7	0.70312	0.32842	-0.01619
C8	0.53806	0.06364	0.15446
O1	0.7413	0.3203	0.00001
N1	1.02357	0.52232	0.04132
N2	0.71099	0.37335	-0.01772
H1	0.81767	0.3222	-0.25169
H2	0.90458	0.38799	-0.19275
H3	0.85753	0.47181	0.41036
H4	0.77338	0.40665	0.36504
H5	1.05628	0.49171	0.30545

Table S2 Fractional atomic coordinates for the unit cell of TPHH-COF calculated based on staggered AB model.

Space group	P6 ₃		
Unit cell	$a = b = 28.3805 \text{ \AA}, c = 6.0482 \text{ \AA}, \alpha = \beta = 90^\circ, \gamma = 120^\circ$		
atom	x	y	z
C1	1.03923	0.88073	1.57785
C2	0.28751	0.62687	0.50228
C3	0.17962	0.78893	0.84828
C4	0.22337	0.78408	0.76545
C5	0.71303	0.8783	1.26517
C6	0.76684	0.91873	1.31437
C7	0.80183	0.9558	1.15571
C8	0.78809	0.92264	1.52721
C9	0.21832	0.75881	0.56051
C10	0.8555	0.99311	1.20411
C11	0.87658	0.99536	1.4148
C12	0.27287	0.8035	0.87877
C13	0.96462	1.01352	1.46089
C14	0.25992	0.75242	0.47312
C15	0.31462	0.79715	0.79337
C16	0.30849	0.7709	0.59074
O1	0.23531	0.58516	0.51323
O2	0.9294	1.03261	1.4598
N1	-0.29172	0.32647	0.00377
N2	0.19113	0.36683	1.03781
N3	0.68516	0.87511	1.08849
N4	0.96302	1.0142	0.95987
H1	0.18759	0.54011	0.88525
H2	0.22531	0.36665	0.74439
H3	0.68911	0.8441	1.38842
H4	0.78759	0.9554	0.98674
H5	0.76217	0.89465	1.65763
H6	0.88182	1.02046	1.07318
H7	0.85698	0.96369	1.74619
H8	0.1803	0.74309	0.46581
H9	0.27966	0.8242	1.03886
H10	0.25437	0.73176	0.31328