Supporting Information

Tetraphenylethylene-based Covalent Organic Framework for Waste Gas Adsorption and Highly Selective Detection of Fe^{3+}

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Contents

Section A. Material and methods

Chemicals and Materials: 1,1,2,2-tetraphenylethene, bromine, 4-formylphenylboronic acid, K_2CO_3, NaOH, tetrabutyl ammonium chloride, 4,4'-Diaminodibenzophenone, Raney Nickel, and tetrakis(triphenylphosphine)palladium(0) were purchased from Aladdin and Energy chemical. All solvents used were purchased from Aladdin.

Synthesis of Tetrakis(4-bromophenyl)ethylene (TBTPE)[S1]: Powdered 1,1,2,2-tetraphenylethene (5.00 g, 15.0 mmol) was treated with bromine (7.50 mL, 0.15 mol) and the mixture was kept for 16 h at room temperature. The resulting solid was dissolved in hot toluene (120 mL), concentrated to about 20 mL, and the precipitate was isolated. Purification using flash chromatography on SiO_2 (hexanes/CH_2Cl_2, 20:1 in vol.) gives TBTPE as a colorless solid (5.94 g) in 61% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.26 (d, 8H), 6.85 (d, 8H).

Synthesis of 4',4'',4''',4''''-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-4-carbaldehyde)) (TFBPE)[S2]: TBTPE (684 mg, 1 mmol) and 4-formylphenylboronic acid (900 mg，6 mmol) was dissolved in toluene (80 mL), and then an aqueous solution of K_2CO_3 (1.66 g, 12 mmol) in water (15 mL) and tetrabutyl ammonium chloride (1 mL) were added. Then $Pd(PPh_3)_4$ catalyst (10 mg) was added and the reaction mixture was stirred at 85 °C for 1 d. After cooling to room temperature, the reaction mixture was mixed with water and the organic layer was precipitated by CH_3OH to get crude product. Recrystallization with $CHCl_3$ and diethyl ether to obtain yellowish green solid (535 mg, 71%). ^{1}H NMR (DMSO-d_6 400 Hz): δ (ppm) 10.03 (s, 4H), 7.96 (d, 8H), 7.90 (d, 8H), 7.69 (d, 8H), 7.24 (d,8H).

Synthesis of 1,1,2,2-Tetrakis(4-aminophenyl)ethene (TAPE)[S3]: Weigh 4,4'-

Diaminodibenzophenone (0.3 g, 1.41 mmol) and Raney Nickel (0.4 g, 3.37 mmol), slowly add the mixture of 48% HBr (10 mL) and concentrated HCl (10 mL) to the mixture, and stir at 100 ℃ for 5 hours. Once the reaction is complete, cool to room temperature, add 100 ml saturated NaOH solution, and stir for 1 hour. The solid sediment was collected and the title compound (0.23 g, 0.60 mmol, 85 %) as a yellow powder. ^{1}H NMR (DMSO-d_6 400 Hz): δ (ppm) 6.57 (d, 8 H), 6.26 (d, 8H), 4.85 (s, 8H).

Synthesis of TTPE-COF: A 10 mL pyrex tube is charged with TAPE (9.8 mg, 25 μmol), TFBPE (18.7 mg, 25 μmol), 3 mL of anhydrous toluene / anhydrous acetonitrile （v/v=3:2）, and 0.2 mL of 6 M aqueous acetic acid. This mixture was sonicated for 20 minutes to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 5 days. The precipitation was collected by centrifugation, washed repeatedly with anhydrous acetone and then dried at 120 °C under vacuum for 12 hours to give a yellow powder (21 mg, 76%).

Material Characterization: Fourier transforms Infrared (FT-IR) spectra were recorded on a Perkin-Elmer model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, and the pressed product can be directly tested. UV-Vis-IR diffuse reflectance spectra (Kubelka-Munk spectrum) were recorded on a JASCO model V-770 spectrometer equipped with integration sphere model ISN-923. For the UV test, the blank sample test is first carried out with whiteboard as the background, and then the holder with the sample was installed on the window of the integrating sphere. Photoluminescence spectra were recorded on JASCO model FP-8600 spectrofluorometer.

The absolute quantum yield was determined by standard procedure with an integral sphere JASCO model ISF-834 mounted on the FP-8600 spectrofluorometer. Time-resolved fluorescence spectroscopy of solid samples was recorded on Hamamatsu compact fluorescence lifetime spectrometer Quantaurus–Tau model C11367-11. Solid-state ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) analysis was conducted using a AVANCEIII/WB-400. Elemental analysis (C, H, and N) was performed on a Euro Vector EA3000 elemental analyzer. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) was performed using a JEOL JEM 2100 with an acceleration voltage of 300 kV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from 2θ = 2.5° up to 40° with 0.02° increment. TGA analysis was carried out by using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of 5 °C min^{-1} under a nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with Bel Japan Inc. model BELSORP-max analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. Water, benzene and toluene vapor sorption isotherms were collected at 20 °C (293K) from Bel Japan Inc. model BELSORP-max analyzer. All the samples were degassed at 120 °C for 10 h before being subject to vapor sorption measurements. Carbon dioxide sorption isotherms were measured at 318 K and 45 bar with an iSorbHP2 analyzer. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Fluorescence detection: In a typical experimental setup, 3 mg of TTPE-COF was added into the cuvette containing 3 mL of ethanol, and then sonicated to form homo-disperse suspension (1 mg mL^{-1}). Take 0.75 mL of TTPE-COF suspension and add different nitrate (M = Na^+, K^+, Al^{3+}, Cr^{3+}, Cu^{2+}, Hg^+, Hg^{2+}, Bi^{3+}, Fe^{3+}, 1×10^{-2} mol L^{-1}) ethanol solutions to 3 mL. After ten minutes of ultrasonic treatment, the mixed suspension was obtained for fluorescence detection. Will TTPE-COF (3 mg) is added to the 3 ml of different organic solvents, such as Dioxane, H_2O, N,N-Dimethylformamide (DMF), Ethyl acetate (EAC). TTPE-COF solvent suspension was prepared after 10 minutes of ultrasonic treatment for fluorescence detection. The dispersible nature of TTPE-COF will facilitate vicinal contact between the probe and nitro explosive analytes. All the experiments were performed in triplicate and consistent results were reported.

The fluorescence quenching was analyzed using the Stern-Volmer equations:[S4]

$$I_0/I = 1 + K_{sv}[Q]$$

where I_0 and I are the fluorescence intensity, in the absence and presence of the analyte, respectively, K_{sv} is the Stern-Volmer quenching constant and [Q] is the concentration of analyte. The quenching percentage was calculated using the equation as follows:

$$\text{Fluorescence quenching } \% = (1 - I/I_0) \times 100\ \%$$

where I_0 is the initial fluorescence intensity in the absence of metal ions, I is the fluorescence intensity in the presence of the corresponding analyte.

The limit of detection concentration (LOD) was calculated according to the formula:[S5]

$$LOD = 3\delta / K_{sv}$$

and δ is the standard deviation of the detection method.

Regeneration tests： Fluorescence spectra were recorded after the addition of solution contains Fe^{3+} ion. After the fluorescence test, the Fe^{3+} ion was removed by centrifuging 5 min, washing with EtOH three times. The re-generate TTPE-COF suspension was obtained after 3 mL EtOH was added to the precipitant. Fluorescence spectra have recorded the performance of the regenerate TTPE-COF.

Variable temperature fluorescence spectrum: The sample was tested on JASCO model FP-8600 fluorescence spectrometer. The high-temperature fluorescent controller (HPC-836) is used to adjust the ambient temperature. The temperature was controlled within the range of 303 K-573 K. The temperature was raised once every 30°C and kept for 2 minutes. The measurement was made after the temperature was stable.

Section B. TGA curves

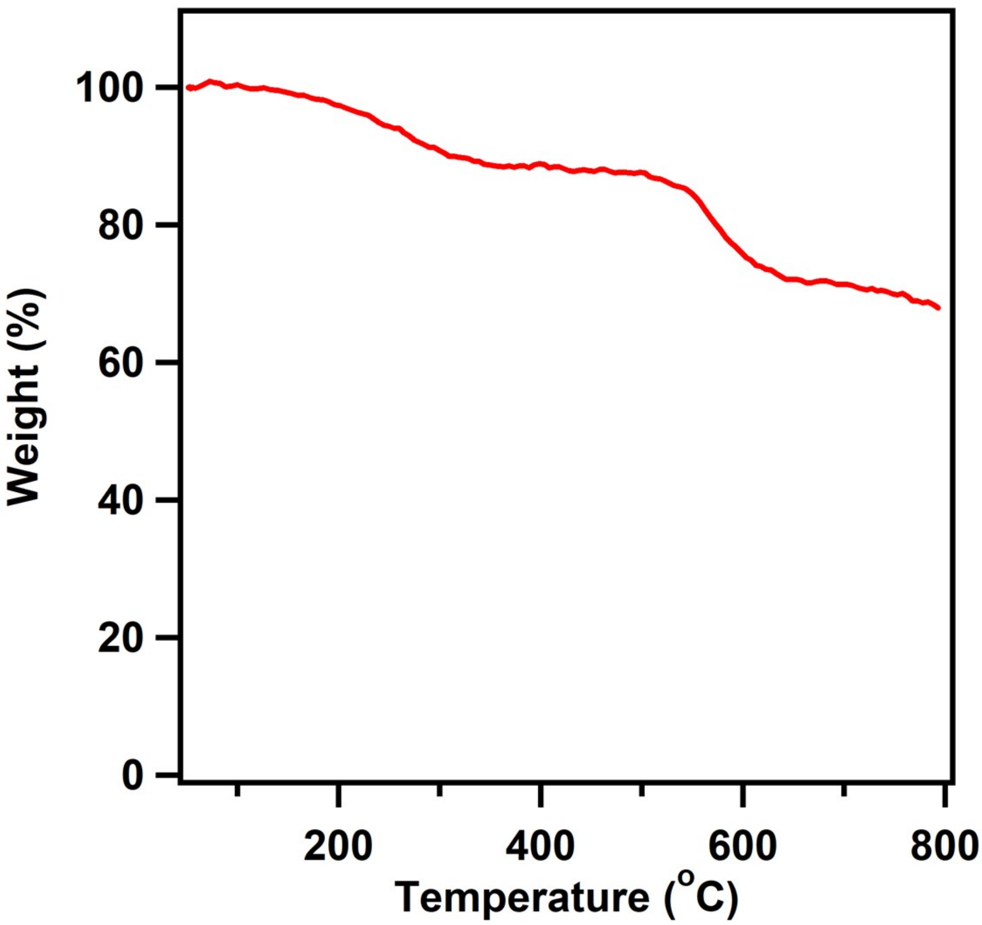

Fig. S1 TGA curve of TTPE-COF.

Section C. SEM images

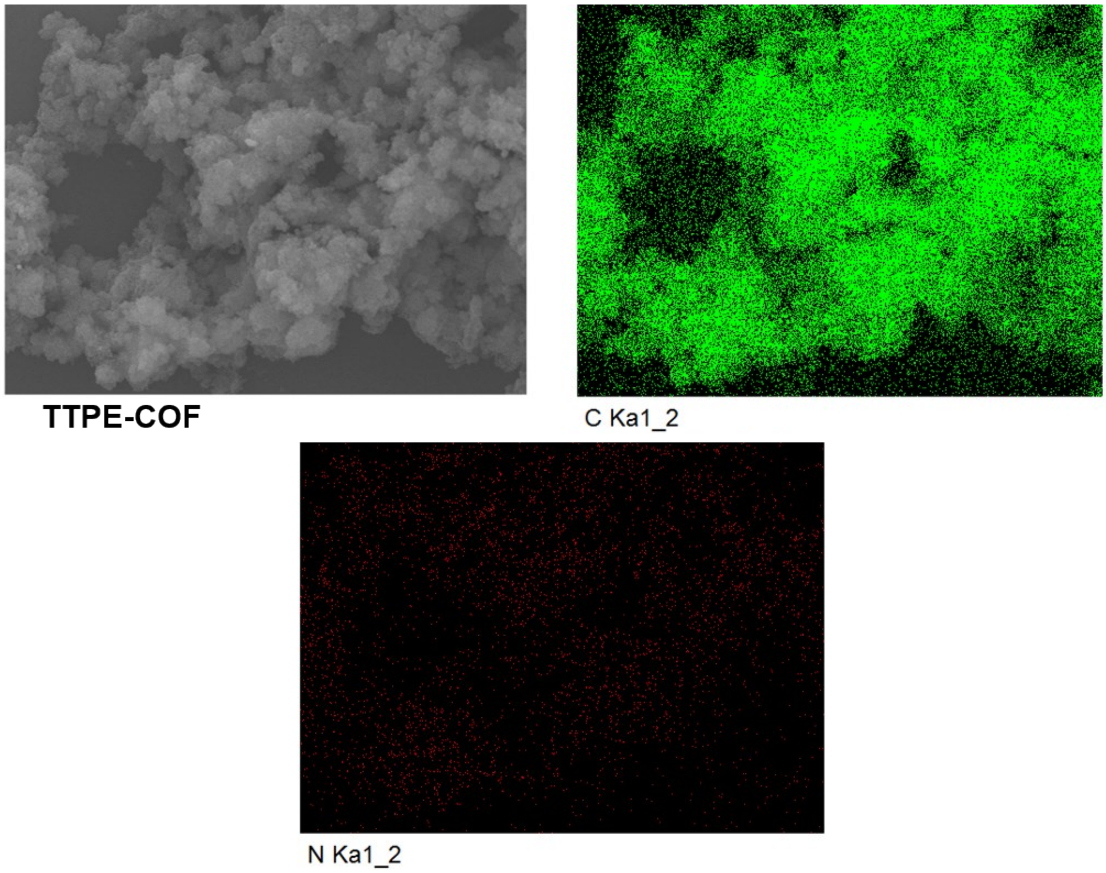

Fig. S2 Energy dispersive spectrometer of TTPE-COF.

Section D. Heat of CO_2 adsorption

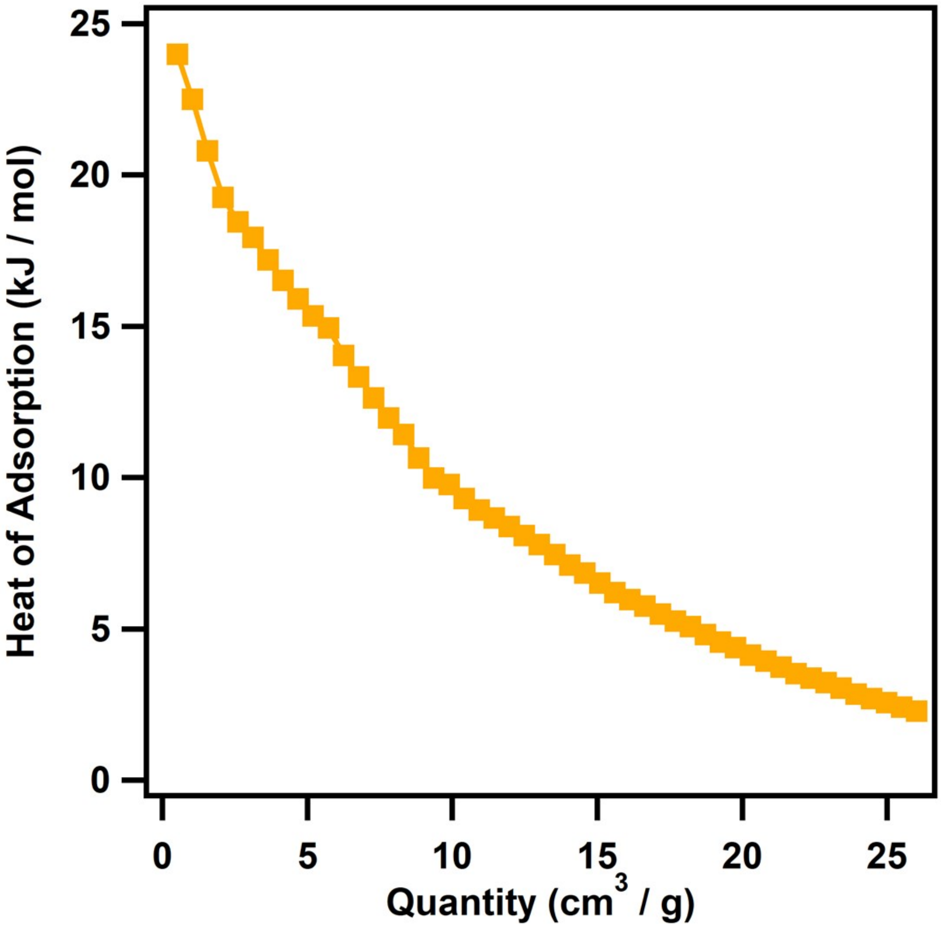

Fig. S3 The isosteric heats of CO_2 adsorption for TTPE-COF.

Section E. The Solid-UV spectra

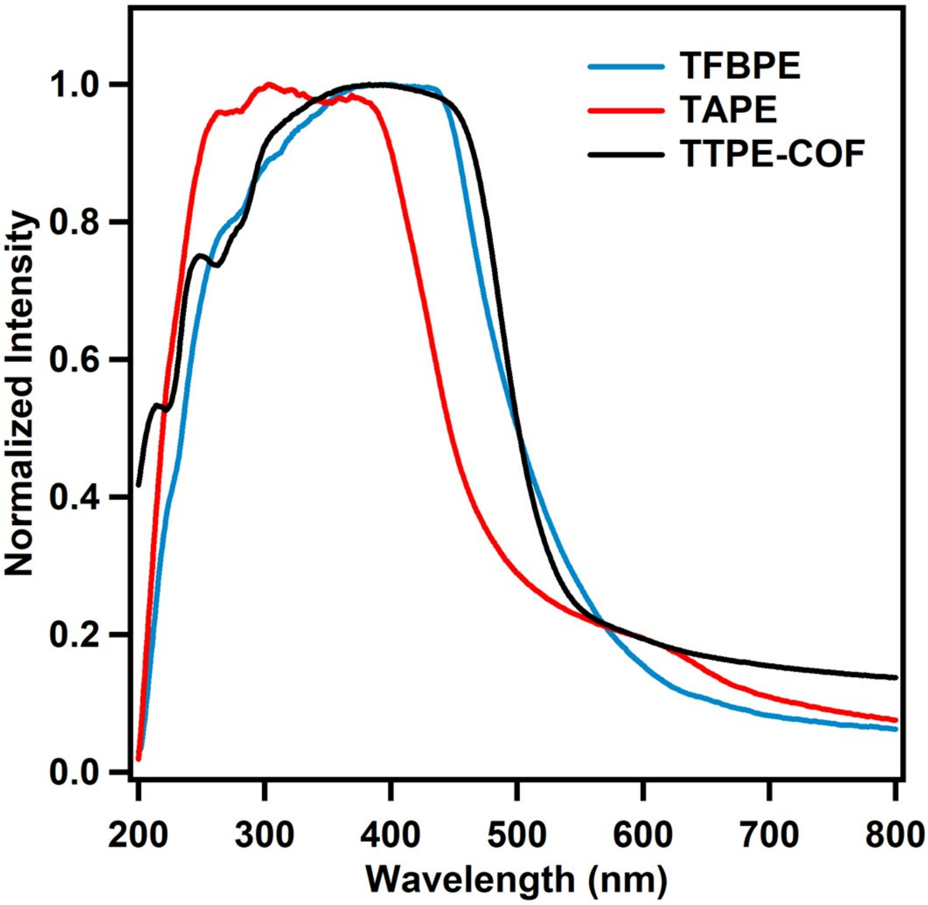

Fig.S4 Solid state UV spectra of TFBPE, TAPE and TTPE-COF.

Section F. Fluorescence emission spectra

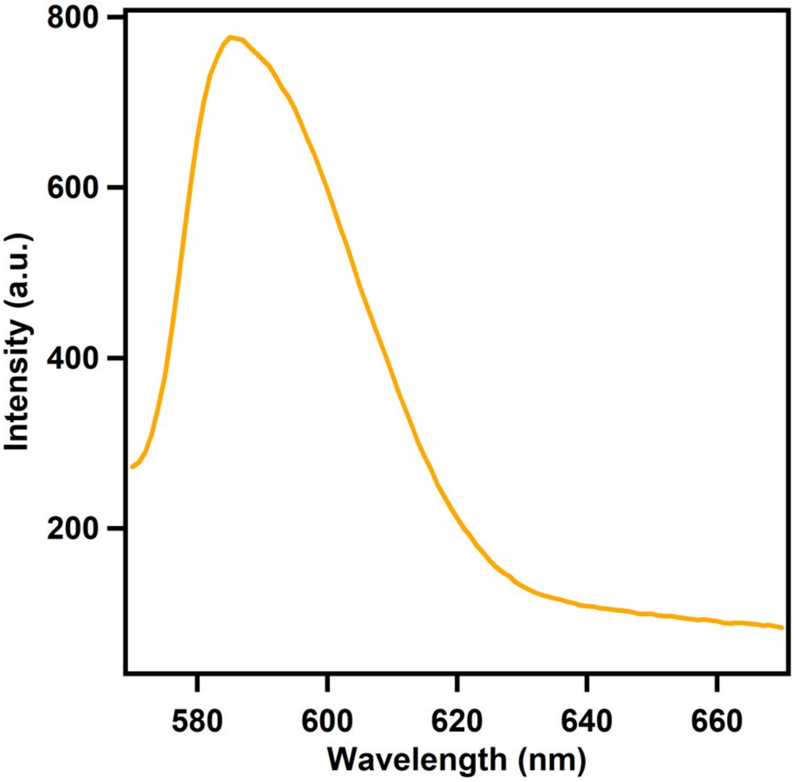

Fig. S5 The solid-state fuorescence spectra of the TTPE-COF.

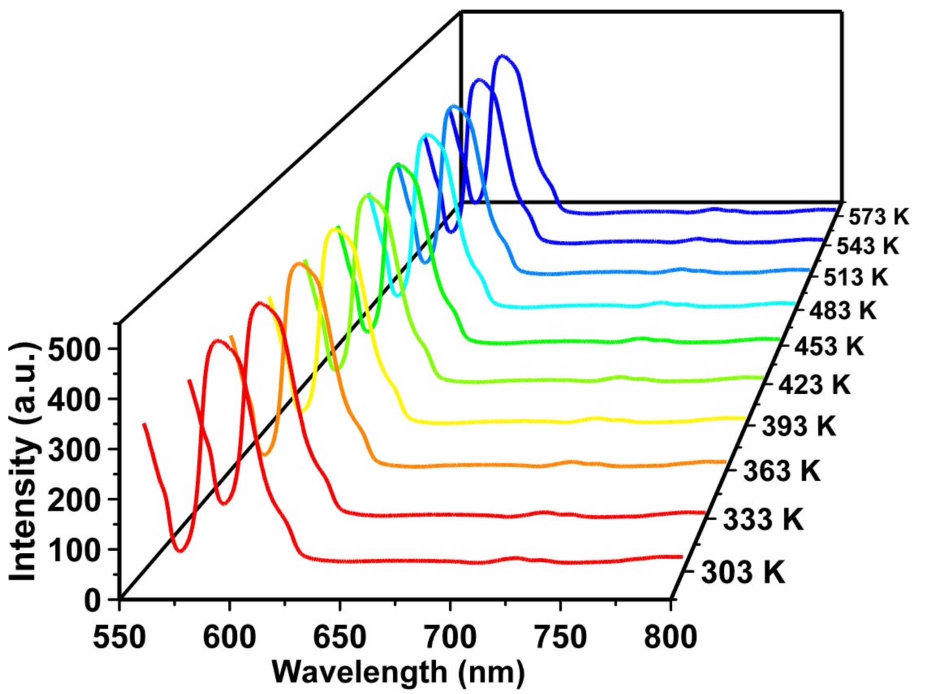

Fig. S6 Variable temperature fluorescence spectra of TTPE-COF.

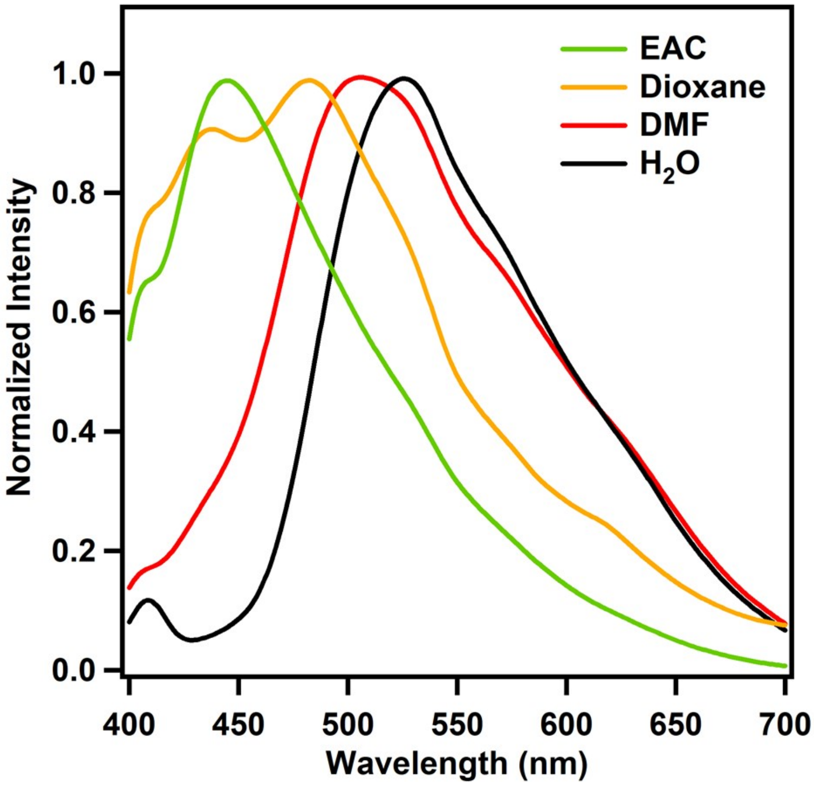

Fig. S7 Fluorescence spectra of TTPE-COF in solvents with different polarities.

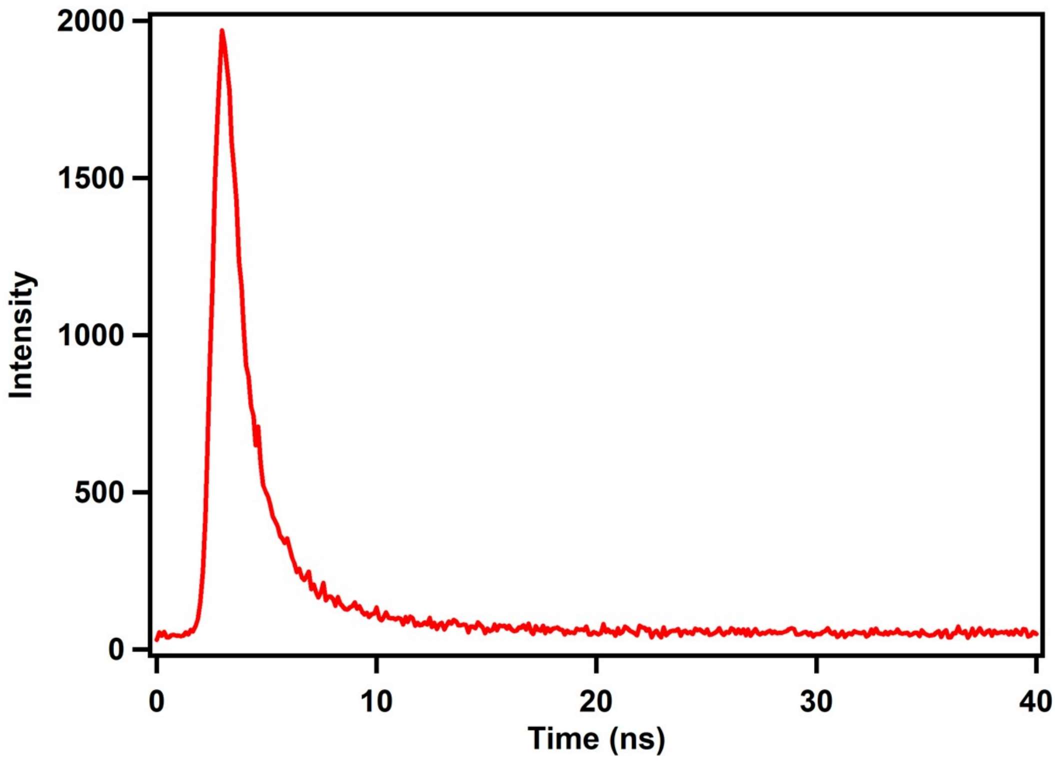

Fig. S8 Time-resolved fluorescence decay profiles of TTPE-COF.

Section G. Stern–Volmer plot curve

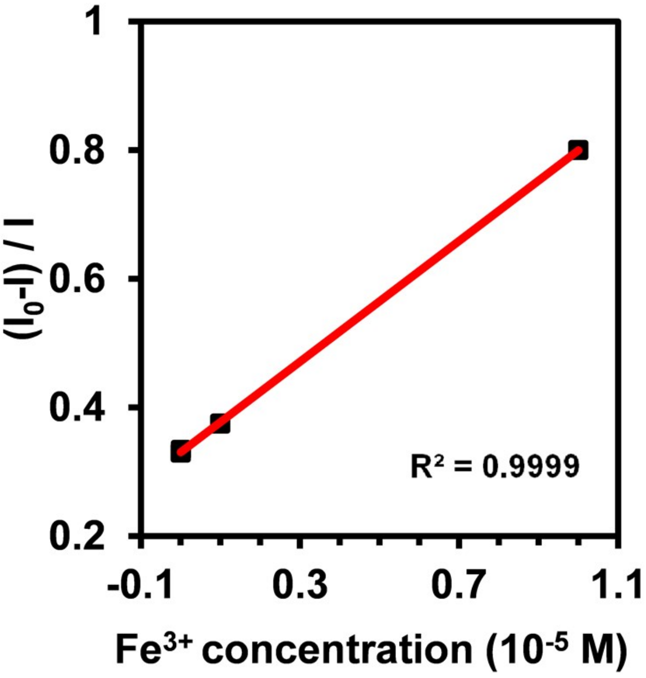

Fig. S9 Stern–Volmer plot curve (10^{-8}-10^{-5} M).

Section H. Selectivity and cyclicality

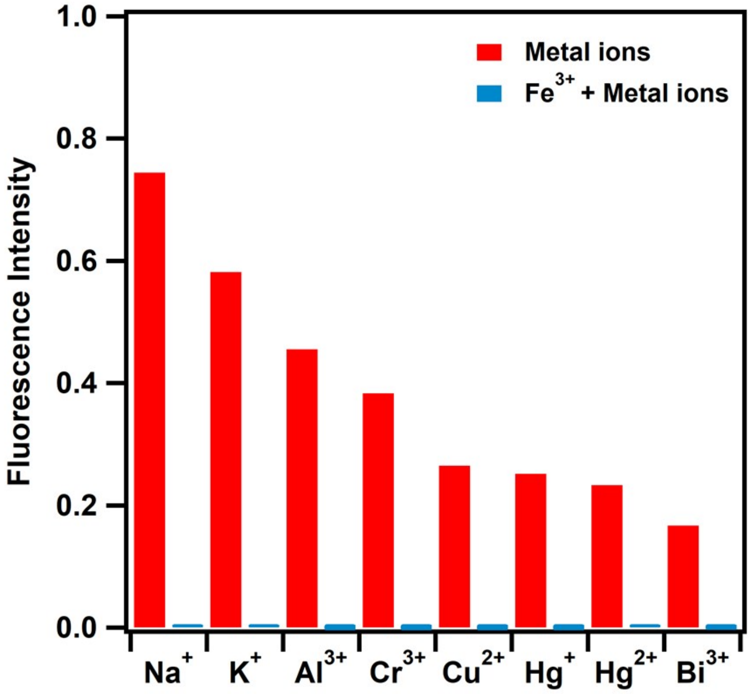

Fig. S10 The PL intensities of TTPE-COF before and after addition of Fe^{3+} in the presen ce of various metal ions.

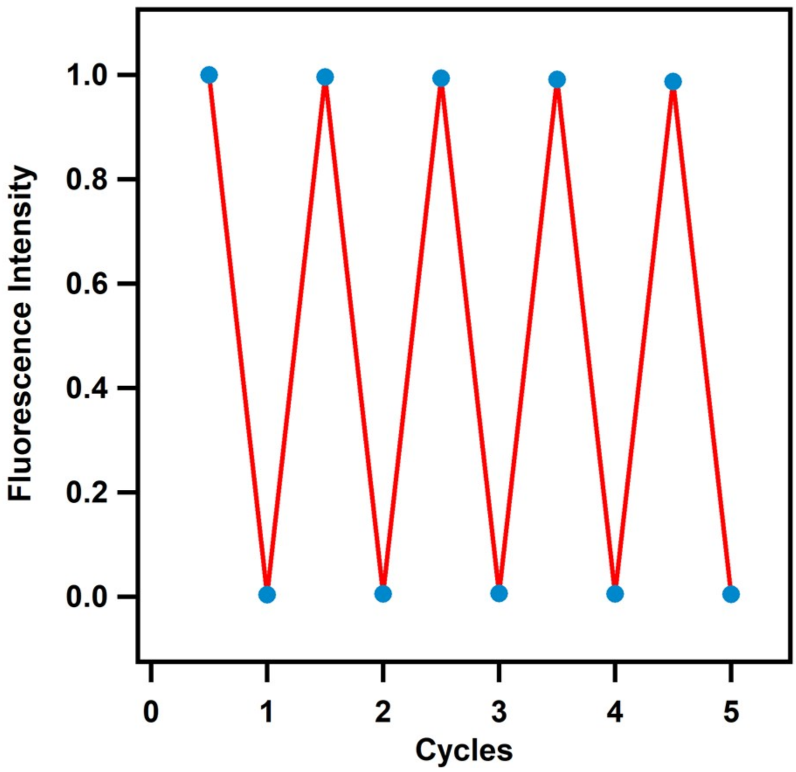

Fig. S11 Quenching and recovery tests of TTPE-COF for Fe^{3+}.

Section I. SEM and FTIR before and after recovery

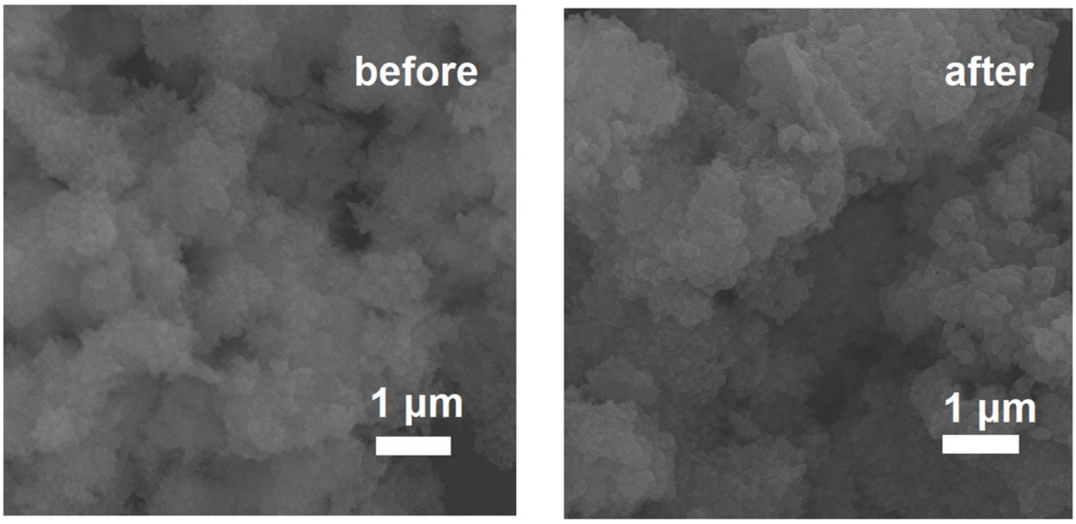

Fig. S12 SEM of TTPE-COF before and after recovery.

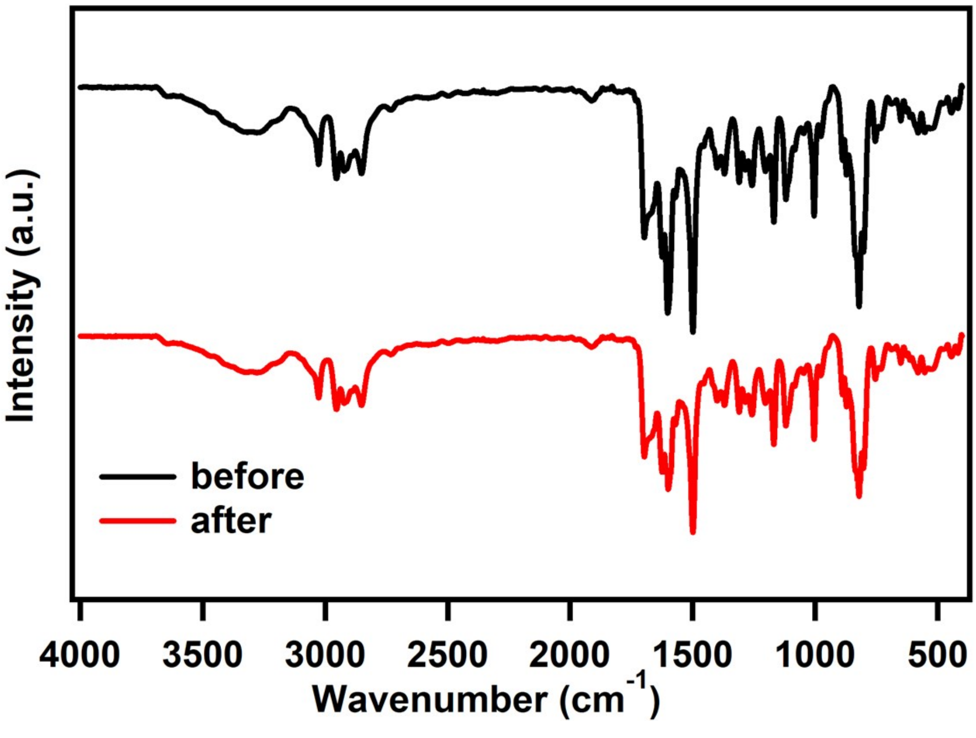

Fig. S13 FTIR of TTPE-COF before and after recovery.

Section J. Unit cell parameters and fractional atomic coordinates

Table S1. Unit cell parameters and fractional atomic coordinates for TTPE-COF.

Space group		*P1*	
Calculated unit cell		a = 34.67 Å, b = 34.69 Å, c = 5.33 Å; α = 69 °, β = γ = 110 °	
Pawley refinement		Rwp = 4.88%, Rp = 3.78%	
atoms	**x**	**y**	**z**
C1	7.31408	0.13695	-0.12106
C2	7.8742	0.06411	-0.06115
C3	7.12927	0.31112	0.10555
C4	7.54939	0.37358	-0.00856
C5	7.8119	0.63292	0.0821
C6	7.36827	0.55174	0.01748
C7	7.62876	0.81449	-0.06684
C8	7.06055	0.87805	0.07996
N9	7.84987	0.02643	0.01655
N10	7.33557	0.15863	0.06349
N11	7.51243	0.34601	-0.04617
N12	7.84308	0.6657	0.13482
N13	7.15737	0.33816	-0.02523
N14	7.02271	0.85405	-0.00067
N15	7.34093	0.51472	0.05759
N16	7.66137	0.84579	-0.12017
C17	7.90651	0.84385	-0.17936
C18	7.94581	0.84	-0.16982
C19	7.98339	0.85856	0.00287
C20	7.98132	0.8801	0.17559
C21	7.94191	0.88305	0.17197

C22	7.8005	0.76169	-0.11916
C23	7.80386	0.72141	-0.09114
C24	7.83741	0.70586	0.11198
C25	7.86719	0.73098	0.28654
C26	7.86363	0.77126	0.25956
C27	7.8788	0.94574	-0.15776
C28	7.8758	0.98506	-0.16064
C29	7.85427	0.98713	0.01193
C30	7.83565	0.94959	0.18334
C31	7.83956	0.91037	0.19214
C32	7.85987	0.90786	0.01392
C33	7.90398	0.86409	-0.00062
C34	7.83105	0.78764	0.04941
C35	7.86205	0.86602	0.00667
C36	7.82741	0.83125	0.00665
C37	7.72651	0.87013	-0.2732
C38	7.70165	0.8404	-0.09786
C39	7.71759	0.80719	0.10573
C40	7.75799	0.8041	0.13343
C41	7.78367	0.83459	-0.03598
C42	7.76693	0.86685	-0.24653
C43	7.82149	0.13533	0.03186
C44	7.82897	0.0991	0.01916
C45	7.86611	0.10199	-0.04398
C46	7.89591	0.14157	-0.09067
C47	7.88881	0.17771	-0.07362
C48	7.65989	0.39145	-0.07554
C49	7.6237	0.39895	-0.06064
C50	7.58735	0.36525	-0.0249

C51	7.5879	0.32386	-0.00255
C52	7.62443	0.31622	-0.01105
C53	7.86758	0.55647	0.08347
C54	7.86084	0.59331	0.09313
C55	7.82019	0.59381	0.08703
C56	7.78653	0.55687	0.07405
C57	7.79334	0.51994	0.06717
C58	7.8513	0.17514	-0.01459
C59	7.66061	0.34998	-0.04845
C60	7.83385	0.5195	0.07012
C61	7.92222	0.3384	0.29881
C62	7.96137	0.33298	0.31791
C63	7.97944	0.35124	0.09095
C64	7.95831	0.37669	-0.14986
C65	7.91905	0.38179	-0.16874
C66	7.81212	0.2489	0.16942
C67	7.82051	0.21222	0.1707
C68	7.84278	0.214	-0.0099
C69	7.85587	0.25319	-0.1931
C70	7.84713	0.28962	-0.19536
C71	7.86983	0.44443	-0.11931
C72	7.86394	0.48183	-0.11162
C73	7.84087	0.48032	0.0627
C74	7.82468	0.44106	0.23297
C75	7.83131	0.40391	0.22899
C76	7.85237	0.40467	0.04466
C77	7.90025	0.36229	0.05447
C78	7.8269	0.28854	-0.00591
C79	7.85649	0.36415	0.02782

C80	7.82222	0.32892	0.00955
C81	7.71849	0.36229	-0.26791
C82	7.69986	0.34174	-0.04495
C83	7.72002	0.31472	0.18898
C84	7.75917	0.30972	0.20502
C85	7.77841	0.33063	-0.01616
C86	7.75717	0.35636	-0.25434
C87	7.37052	0.05059	0.07141
C88	7.36162	0.08723	0.06756
C89	7.32388	0.09798	-0.10731
C90	7.29507	0.07135	-0.27616
C91	7.30333	0.03419	-0.26729
C92	7.34131	0.02324	-0.09452
C93	7.0253	0.30101	0.23446
C94	7.06128	0.29142	0.23522
C95	7.09136	0.3222	0.09879
C96	7.08492	0.36295	-0.03764
C97	7.04901	0.37271	-0.0369
C98	7.01869	0.3418	0.09902
C99	7.51576	0.79528	-0.04884
C100	7.55275	0.78872	-0.05698
C101	7.58957	0.8225	-0.07044
C102	7.5889	0.86302	-0.07558
C103	7.55202	0.8695	-0.06464
C104	7.3108	0.6266	0.02118
C105	7.31845	0.59011	0.01227
C106	7.35986	0.58967	0.0333
C107	7.39357	0.6261	0.06787
C108	7.38606	0.66223	0.08328

C109	7.17409	0.89198	0.09293
C110	7.1381	0.89926	0.11099
C111	7.0983	0.86975	0.06255
C112	7.09505	0.83269	-0.00309
C113	7.13112	0.82502	-0.01674
C114	7.34458	0.66283	0.05778
C115	7.51516	0.83566	-0.05095
C116	7.17113	0.85457	0.03117
C117	7.39619	0.33417	-0.19161
C118	7.43508	0.33081	-0.19459
C119	7.47353	0.35051	-0.03431
C120	7.47283	0.37269	0.13908
C121	7.43386	0.37479	0.15071
C122	7.28845	0.25	-0.09961
C123	7.29191	0.21079	-0.09484
C124	7.32876	0.19702	0.06792
C125	7.36006	0.22156	0.24162
C126	7.35646	0.26083	0.23693
C127	7.37057	0.43609	-0.13349
C128	7.36773	0.475	-0.12613
C129	7.34578	0.47586	0.04797
C130	7.32702	0.43761	0.21318
C131	7.33129	0.39889	0.21482
C132	7.35148	0.39735	0.03194
C133	7.39493	0.35471	-0.00965
C134	7.3218	0.27679	0.05247
C135	7.35345	0.35575	0.01439
C136	7.31891	0.32057	0.01995
C137	7.21762	0.35831	-0.22319

C138	7.19616	0.33118	-0.02166
C139	7.21426	0.29933	0.18396
C140	7.25322	0.29534	0.18787
C141	7.27573	0.32378	-0.00512
C142	7.2569	0.35448	-0.21724
C143	7.39935	0.83283	-0.21081
C144	7.43656	0.82621	-0.21411
C145	7.47589	0.84245	-0.04305
C146	7.47741	0.86548	0.13187
C147	7.43995	0.87135	0.13889
C148	7.30442	0.76129	-0.19241
C149	7.30928	0.72217	-0.17772
C150	7.33637	0.70197	0.05578
C151	7.35711	0.72052	0.2797
C152	7.35135	0.75918	0.26743
C153	7.37737	0.92085	0.18596
C154	7.37323	0.96061	0.16476
C155	7.34937	0.98277	-0.0809
C156	7.33162	0.96471	-0.30891
C157	7.33562	0.9248	-0.28607
C158	7.35814	0.90219	-0.03829
C159	7.40014	0.85394	-0.02647
C160	7.32558	0.78048	0.02962
C161	7.35963	0.85834	-0.01153
C162	7.32419	0.82432	0.00494
C163	7.2492	0.85857	0.20954
C164	7.20981	0.84582	0.02537
C165	7.20764	0.82359	-0.15691
C166	7.24414	0.81489	-0.15617

C167	7.28397	0.82932	0.02028
C168	7.28542	0.84946	0.21136
H169	7.28875	0.14721	-0.29306
H170	7.90172	0.06825	-0.12915
H171	7.1327	0.2795	0.2211
H172	7.5525	0.40387	0.02277
H173	7.7791	0.63377	0.03421
H174	7.39854	0.55492	-0.0146
H175	7.62984	0.78181	-0.01907
H176	7.0649	0.90541	0.1503
H177	7.87799	0.83036	-0.32206
H178	7.94754	0.82311	-0.3003
H179	8.00972	0.89352	0.31863
H180	7.94087	0.89945	0.30839
H181	7.77406	0.77291	-0.27302
H182	7.78097	0.70291	-0.23234
H183	7.89299	0.71902	0.44402
H184	7.88661	0.78989	0.39916
H185	7.89524	0.94473	-0.29388
H186	7.88922	1.01342	-0.30293
H187	7.81874	0.95128	0.31369
H188	7.82609	0.8819	0.33422
H189	7.71425	0.89567	-0.43097
H190	7.69931	0.78437	0.24758
H191	7.76954	0.77793	0.28774
H192	7.78537	0.88979	-0.38659
H193	7.79195	0.13225	0.07269
H194	7.80553	0.06878	0.05559
H195	7.92484	0.14445	-0.13865

H196	7.91286	0.20764	-0.10505
H197	7.68778	0.41776	-0.10131
H198	7.62398	0.43108	-0.07792
H199	7.5602	0.29743	0.02558
H200	7.62453	0.28404	0.01052
H201	7.89916	0.55667	0.08889
H202	7.88712	0.62166	0.10126
H203	7.75493	0.55667	0.06837
H204	7.76682	0.49184	0.05488
H205	7.90885	0.32353	0.47424
H206	7.97742	0.3143	0.51009
H207	7.97101	0.39091	-0.32969
H208	7.9025	0.39906	-0.36379
H209	7.7954	0.24592	0.31387
H210	7.81044	0.18266	0.31815
H211	7.87189	0.25537	-0.34049
H212	7.85596	0.31888	-0.34665
H213	7.88709	0.44702	-0.25992
H214	7.87649	0.51185	-0.24686
H215	7.80783	0.43957	0.37414
H216	7.82041	0.37446	0.37244
H217	7.70311	0.38299	-0.45146
H218	7.70639	0.29917	0.36498
H219	7.77524	0.29149	0.39725
H220	7.77095	0.37255	-0.42751
H221	7.4005	0.04406	0.20299
H222	7.3844	0.10758	0.19827
H223	7.26574	0.07903	-0.41284
H224	7.27939	0.01371	-0.39278

H225	7.00219	0.27617	0.33577
H226	7.06555	0.25977	0.34176
H227	7.10783	0.38721	-0.14347
H228	7.04518	0.40455	-0.14061
H229	7.48774	0.76868	-0.0364
H230	7.55269	0.75722	-0.05198
H231	7.61717	0.88939	-0.084
H232	7.55207	0.90099	-0.06947
H233	7.27861	0.62661	0.00084
H234	7.29204	0.56235	-0.0149
H235	7.42571	0.62647	0.08415
H236	7.41238	0.69016	0.10843
H237	7.2042	0.91582	0.12565
H238	7.14126	0.92813	0.16092
H239	7.06456	0.80947	-0.04085
H240	7.12775	0.79555	-0.05951
H241	7.36702	0.31971	-0.32565
H242	7.43584	0.31343	-0.32525
H243	7.50217	0.38701	0.27204
H244	7.43403	0.3914	0.28982
H245	7.25974	0.25981	-0.22571
H246	7.26565	0.19167	-0.21843
H247	7.38778	0.21049	0.37597
H248	7.3813	0.27928	0.37085
H249	7.3871	0.43614	-0.27251
H250	7.38138	0.50416	-0.26239
H251	7.30989	0.43832	0.34564
H252	7.31812	0.37006	0.35557
H253	7.2038	0.38267	-0.38362

H254	7.19923	0.27819	0.34609
H255	7.26651	0.2704	0.34381
H256	7.27296	0.37587	-0.37422
H257	7.36984	0.82191	-0.35493
H258	7.43507	0.80938	-0.35559
H259	7.50749	0.87805	0.26773
H260	7.44248	0.88861	0.27969
H261	7.28612	0.77739	-0.38427
H262	7.29359	0.70861	-0.35444
H263	7.37788	0.70512	0.46284
H264	7.36776	0.77292	0.44116
H265	7.39381	0.90389	0.38295
H266	7.3872	0.97288	0.34649
H267	7.31456	0.98132	-0.50612
H268	7.32102	0.91157	-0.46256
H269	7.25171	0.87457	0.35817
H270	7.17793	0.81378	-0.30512
H271	7.24089	0.79819	-0.3017
H272	7.3148	0.85788	0.36386

Section K. Supporting references

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