Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Covalent organic polymer framework with C-C bonds as fluorescent probe for selective iron detection

Ercan Özdemir, Damien Thirion and Cafer T. Yavuz*

Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 305-701 Korea

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CONTENTS

Section A. Elemental Analysis

Table S1. Elemental composition of **COP−100** synthesized in different base solvent combinations

Run	Base/Solvent	C	H	N	O
1	Piperidine/MeOH	77.95	4.19	12.62	5.25
2	NaOH/MeOH	77.91	4.09	11.92	6.08
3	MeONa/MeOH	77.69	4.06	12.05	6.21
4	EtONa/EtOH	75.42	4.21	12.66	7.71
5	tBuOK/tBuOH	77.24	4.70	9.80	8.25
6	tBuOK/THF	75.70	5.13	8.03	11.14

Section B. Dinamic Light Scattering (DLS) measurements

	Average Diameter (nm)	Polydispersity index
Sample 1	1664	0.47
Sample 2	1509	0.42

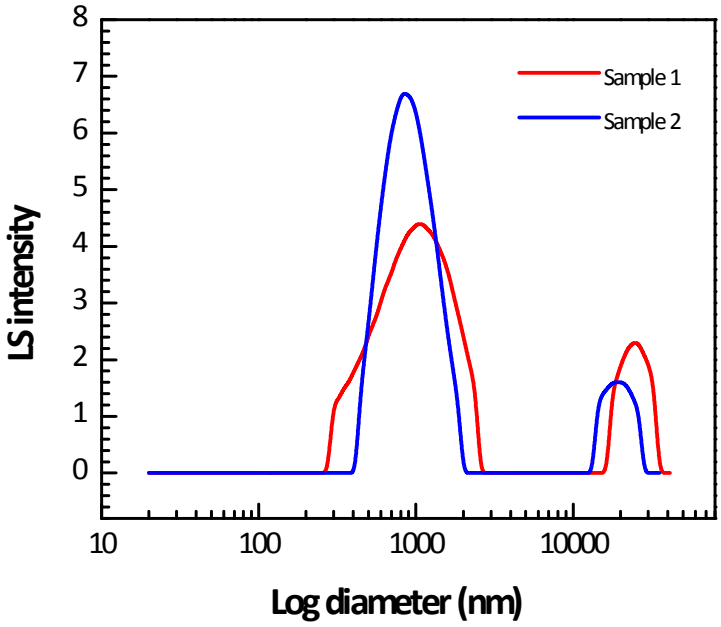


Figure S1. DLS intensity particle size distribution of **COP−100**

Section C. Thermogravimetric Studies

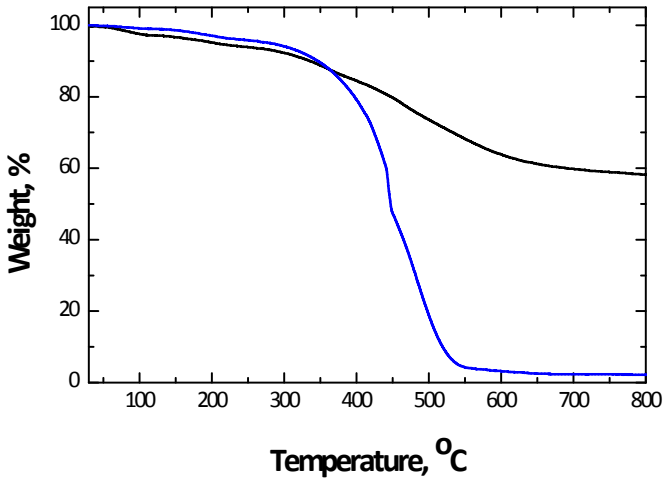


Figure S2. Thermogravimetric profiles of **COP–100** in air (blue) and nitrogen (black)

Section D. Surface Area Measurements

Table S2. Base / solvent effects on textural properties of **COP–100**

Base	Solvents	S_{BET} m^2/g	V_P* cm^3/g	D_P** nm
MeONa	MeOH	4.32	0.0077	8.3
EtONa	EtOH	4.56	0.0199	26.4
Piperidine	MeOH	6.13	0.0522	21.0
t–BuOK	t–BuOH	57.41	0.2216	16.3
t–BuOK	THF	82.26	0.5634	27.4

* Single point adsorption total pore volume of pores

** BJH Desorption average pore diameter (4V/A)

Section E. Absorption spectroscopy

COP–100 (25 mg) was stirred in DMF (100 mL) at 150°C for 24 h to achieve full solubility. Metal ion solutions were prepared from corresponding metal chlorides in 100 mL of DMF with 10 mM concentration.

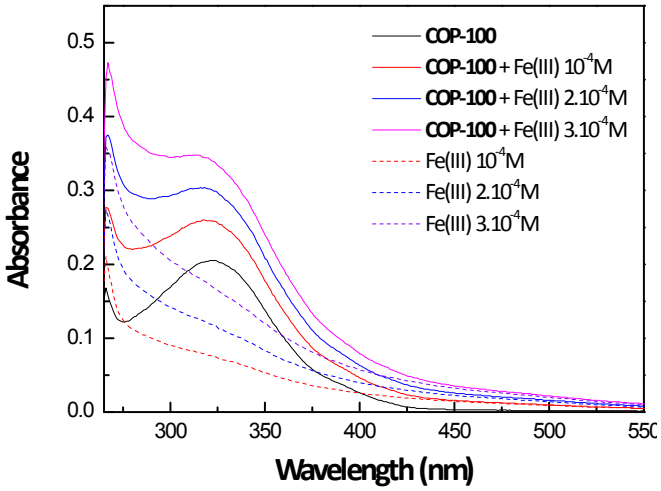


Figure S3. Titration of **COP–100** solution (10 ⍰g/L) with Fe(III). Dashed lines show the absorption of the added Fe(III) solution.

Section F. Fluorescence Quenching–Titrations

Fluorescence emission spectra were recorded at 298 K unless otherwise specified. All titrations were carried out by gradually adding metal ion solutions. Each titration was repeated at least three times to get agreeable. **COP–100** solutions were excited at λ_{exc}=325 nm and their corresponding emission wavelength was monitored from λ = 350 nm to 625 nm. The fluorescence efficiency was calculated by $[(F_o–F)/F_o]\times100$ %, where F_0 and F are the fluorescence intensities of the **COP–100** solution in absence and presence of metal ion, respectively. The slit width for excitation and emission were both set at 15 nm.

Stern−Volmer Plot

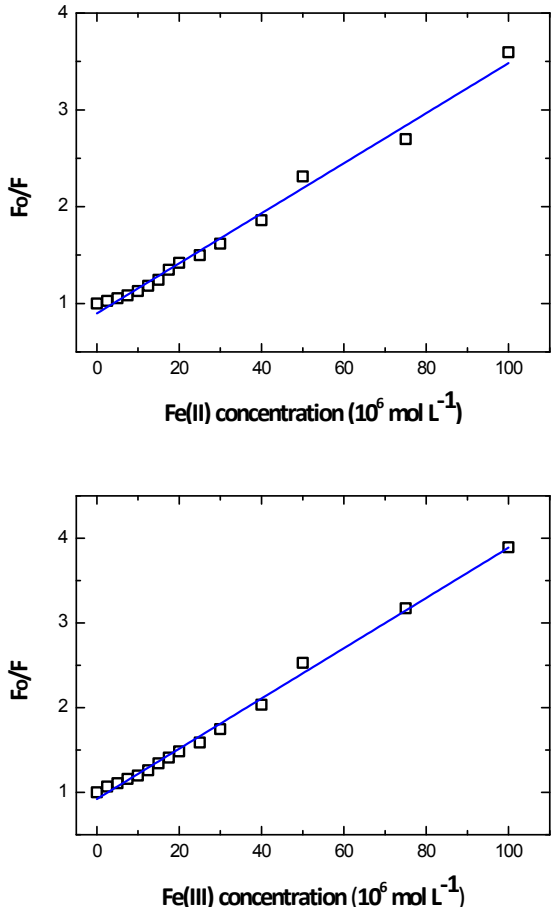


Figure S4. Stern−Volmer plots for the quenching of the emission intensity of **COP−100** by Fe^{2+} and Fe^{3+}

Determination of the detection limit for Fe^{2+} and Fe^{3+}

The detection limits of Fe(II) and Fe(III) were determined according to the work of Huang et al. as follows[1]. Under the same conditions, 5 determinations of the fluorescence emission spectra (λ_{exc}=325 nm) of a blank solvent (DMF) were carried out to obtain the baseline noise. The detection limits, which is the concentration of analyte producing an analytical signal equal to 3 times of the standard deviation of the blank signal, were found to be $2.45.10^{-7}$M for Fe^{2+} and $2.13.10^{-7}$ M for Fe^{3+}.

Fluorescence decay times

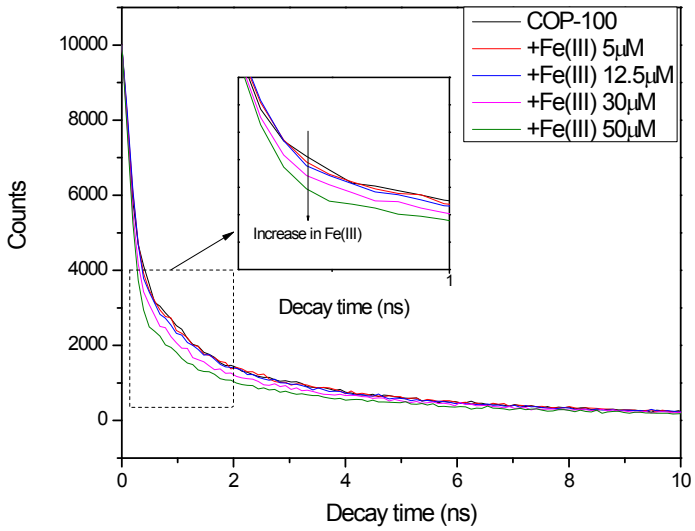


Figure S5. Fluorescence decay times of **COP−100** solution (10 µg/L in DMF) with incremental addition of Fe(III).

The fluorescence decay times have been fitted to a triple exponential function as follows:

$$I(t) = a_1 e^{\frac{-t}{\tau_1}} + a_2 e^{\frac{-t}{\tau_2}} + a_3 e^{\frac{-t}{\tau_3}}$$

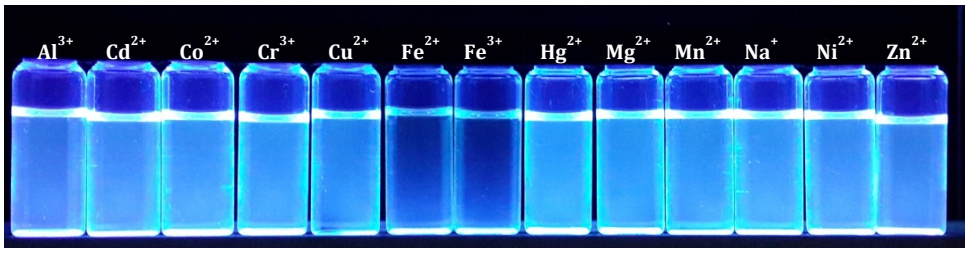
The average lifetime, $\tau_{average}$, is calculated as follows:

$$\tau_{average} = \sum_{i=1}^{3} a_i \tau_i$$

Table S3. Fluorescence decay times of **COP−100** and **COP-100** in the presence of Fe(III)

	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3	$\tau_{average}$ (ns)
COP-100	0.3376	2.4401	9.4449	0.6877	0.2500	0.0623	1.03833161
+Fe(III) 5μM	0.2637	2.1847	9.0788	0.6942	0.2427	0.0630	0.90394203
+Fe(III) 12.5μM	0.2395	2.0774	9.0422	0.7065	0.2348	0.0588	0.83420739
+Fe(III) 30μM	0.2444	2.2324	9.2451	0.7386	0.2078	0.0536	0.80958568
+Fe(III) 50μM	0.2022	2.0844	9.2387	0.7814	0.1778	0.0468	0.67272912

Section G. Fluorescent images of COP-100 solutions



Section H. Supplementary References

1. S. Huang, P. Du, C. Min, Y. Liao, H. Sun and Y. Jiang, 2013, *J. Fluoresc.*, **23**, 621-627.