Supplementary Information

Molecular decoding using luminescence from an entangle porous framework

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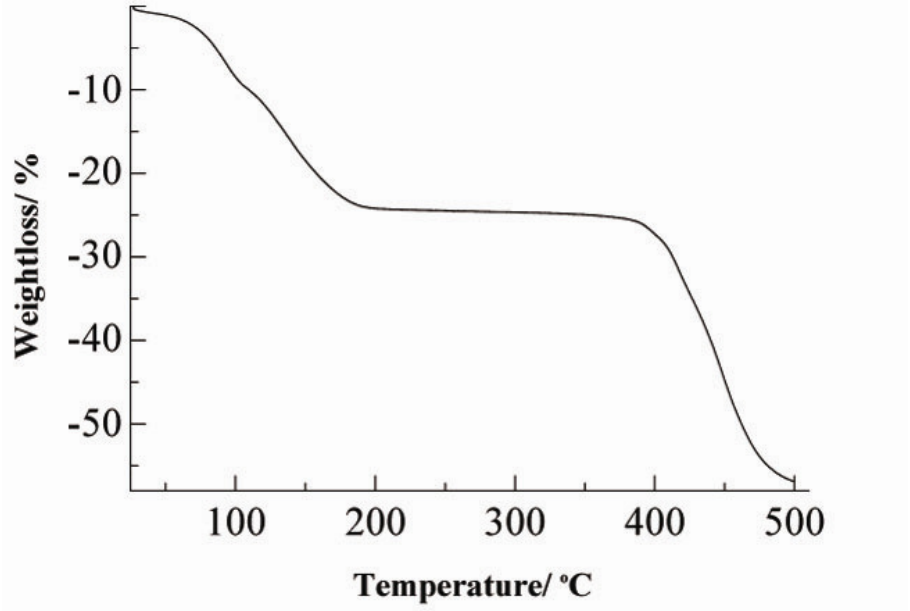
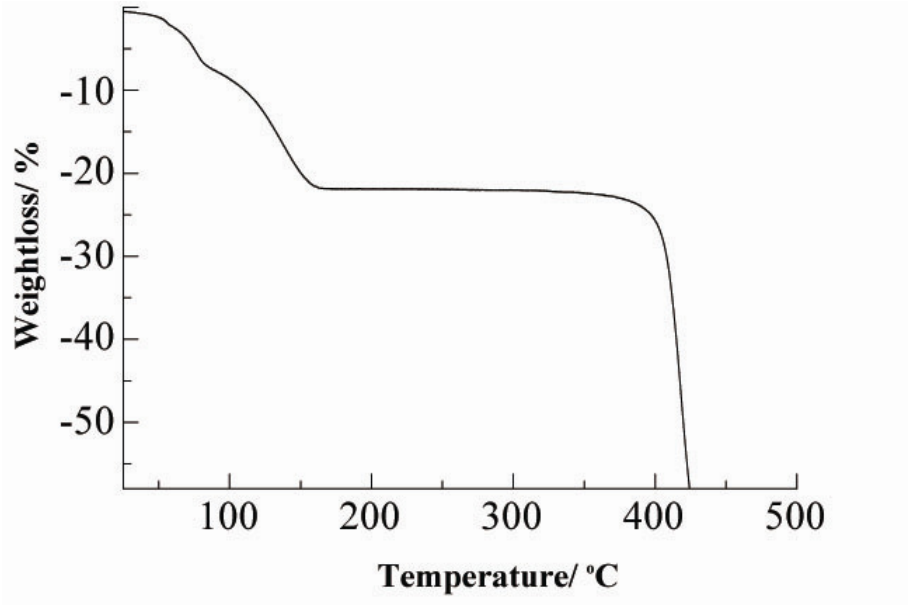
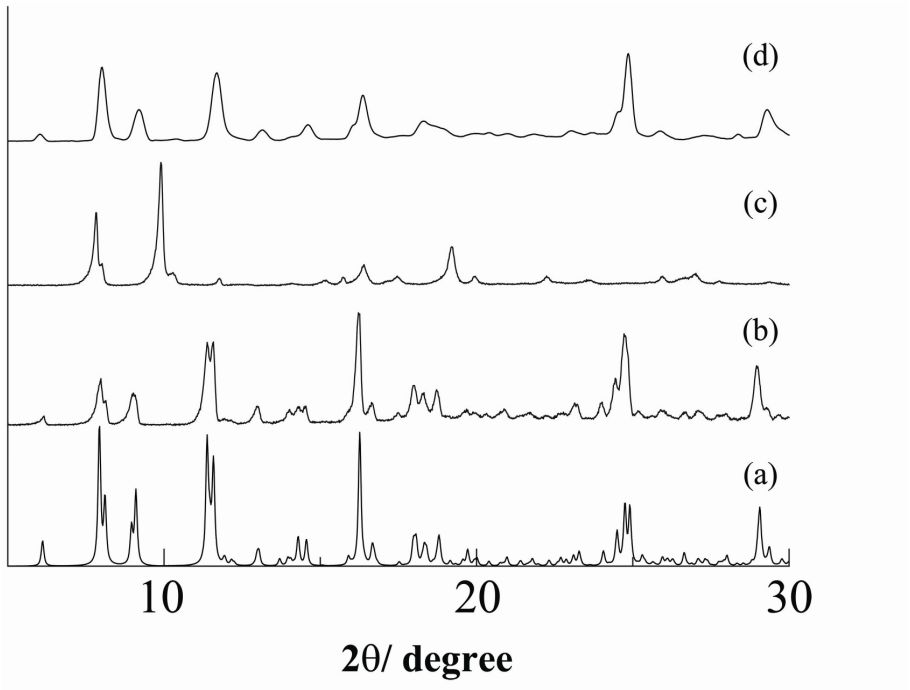


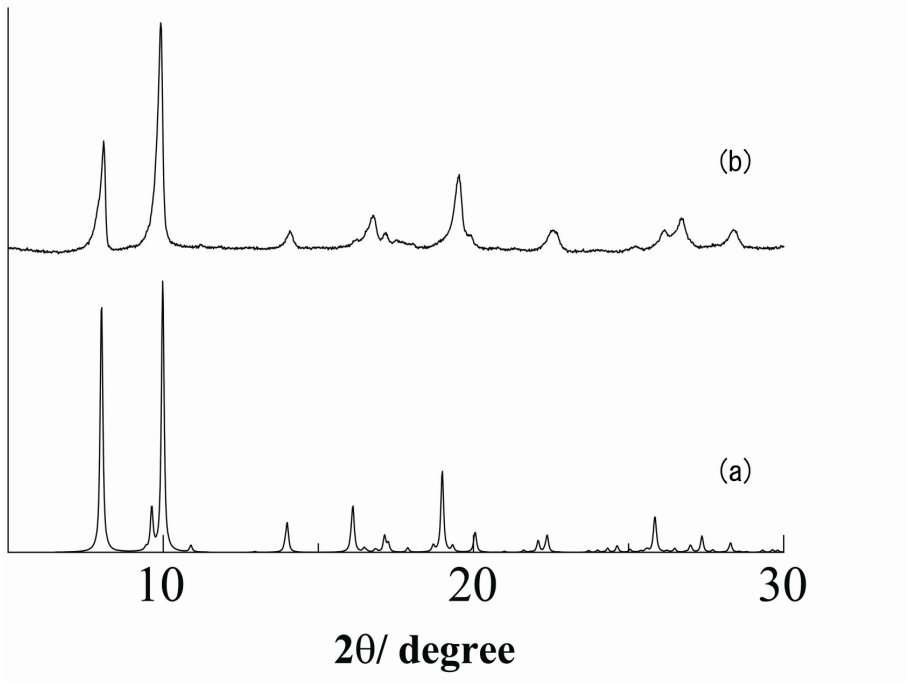
Supplementary Figure S1 | TG analysis showing the weight loss in **1a**. The observed weight loss (24.6 wt%) is the weight of 4 DMF (25.0 wt%).



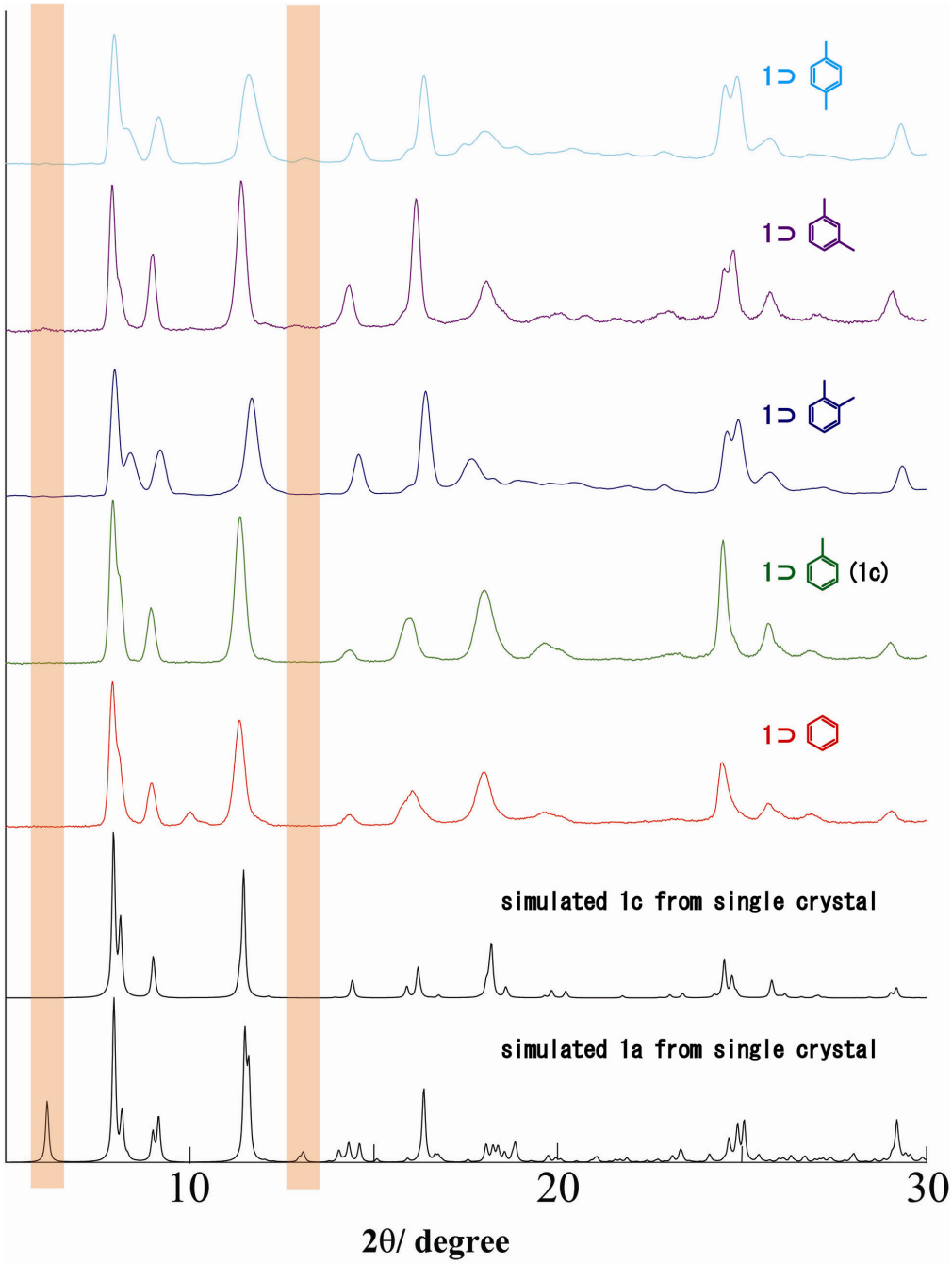
Supplementary Figure S2 | TG analysis showing the weight loss in **1c**. The observed weight loss (21.9 wt%) is the weight of 2.5 toluene (20.8 wt%).



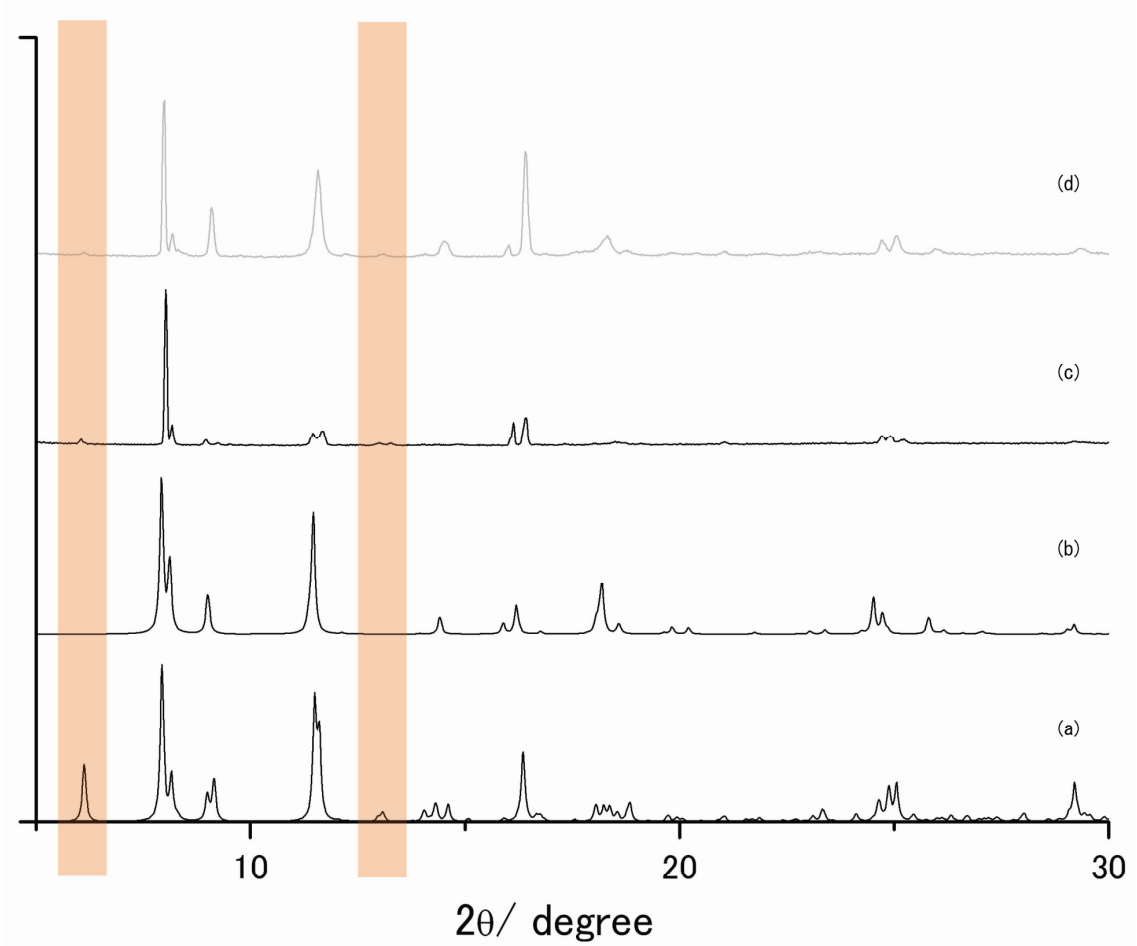
Supplementary Figure S3 I PXRD patterns of **1a**. PXRD patterns of (a) simulated **1a** from single crystal, (b) experimental as synthesized form **1a**, (c) dried form **1**, (d) resolvated form **1a**.



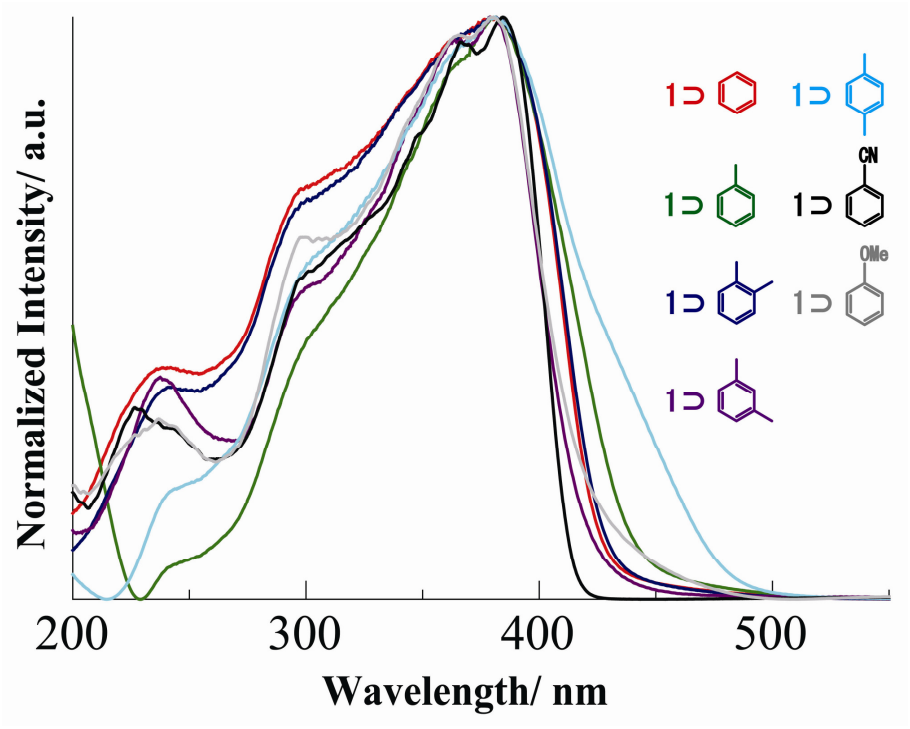
Supplementary Figure S4 | PXRD patterns of **1b**. PXRD patterns of (a) simulated **1b** from single crystal, (b) experimental as dried form **1**. As we show below, the PXRD pattern of **1b** simulated from the single-crystal structure is corresponding to the PXRD pattern of the dried sample of **1** experimentally obtained.



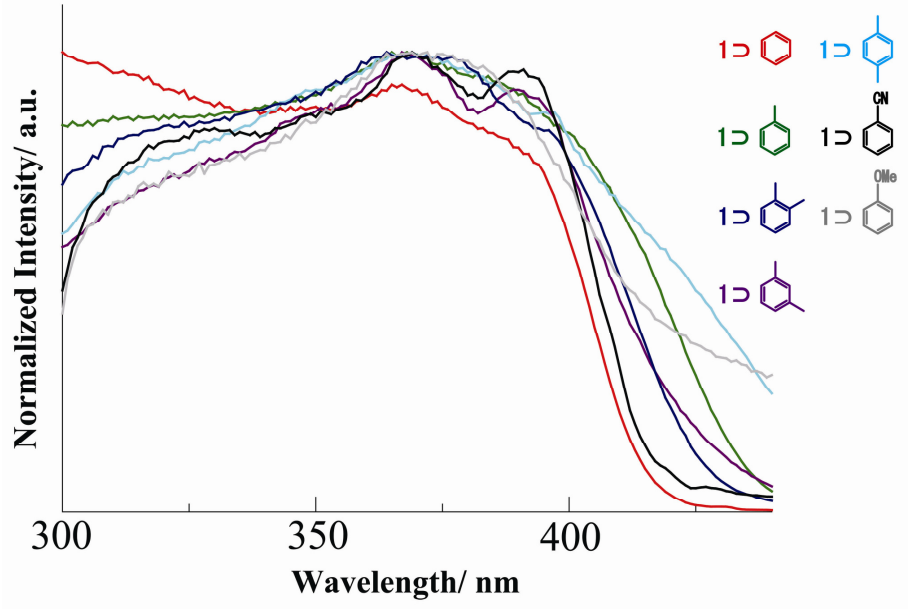
Supplementary Figure S5 | PXRD patterns of **1⊃VOCs**. (Benzene, toluene and *o*-,*m*-,*p*-xylene), showing the **1c** type structure.



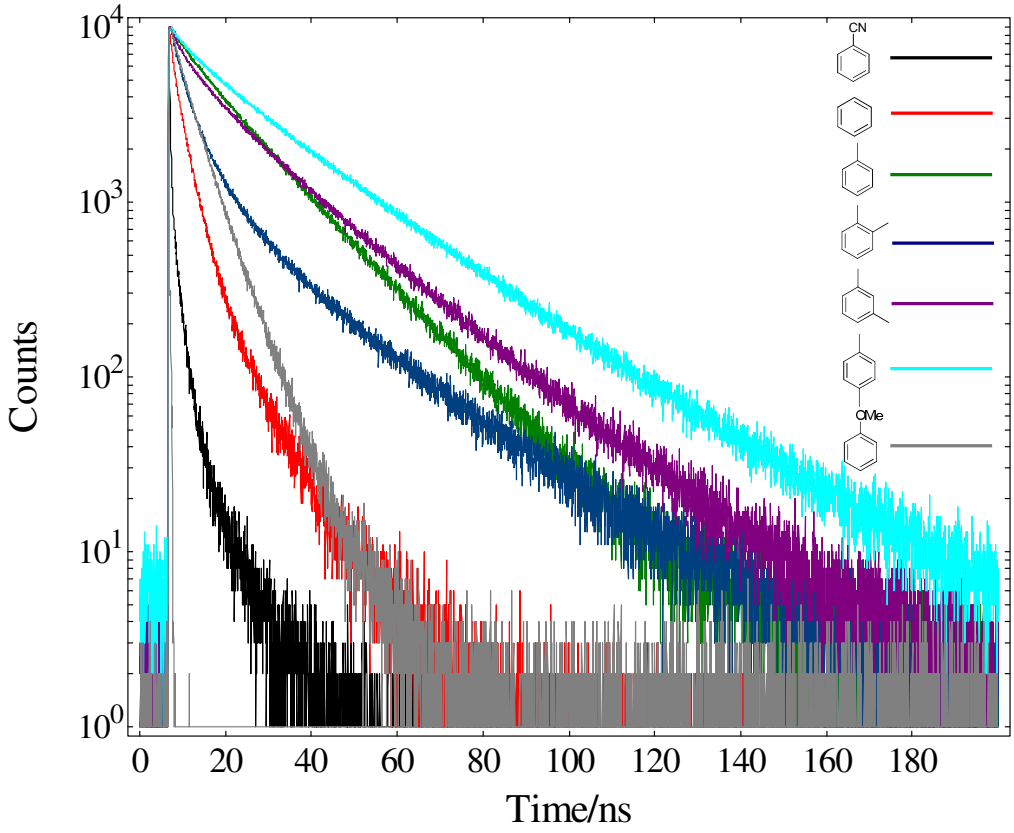
Supplementary Figure S6 I PXRD patterns of (a) simulated **1a** obtained from single crystal determination, (b) simulated **1c** obtained from single crystal determination, (c) **1⊃benzonitrile** and (d) **1⊃anisole**, showing the **1a** type structure.



Supplementary Figure S7 I Diffuse reflectance UV-Vis spectra of **1⊃VOCs**.



Supplementary Figure S8 | Excitation spectra of **1⊃VOCs**. (Benzene, toluene, *o*-, *m*-, *p*-xylene and benzonitrile) detected at 450 nm and **1⊃anisole** detected at 560 nm.



Supplementary Figure S9 I Fluorescence decay curves of **1⊃VOCs**. (Benzene, toluene, *o*-, *m*-, *p*-xylene and benzonitrile). The decay curves were adjusted to a sum of exponential decays (i.e. as multi-exponentials) by means of:

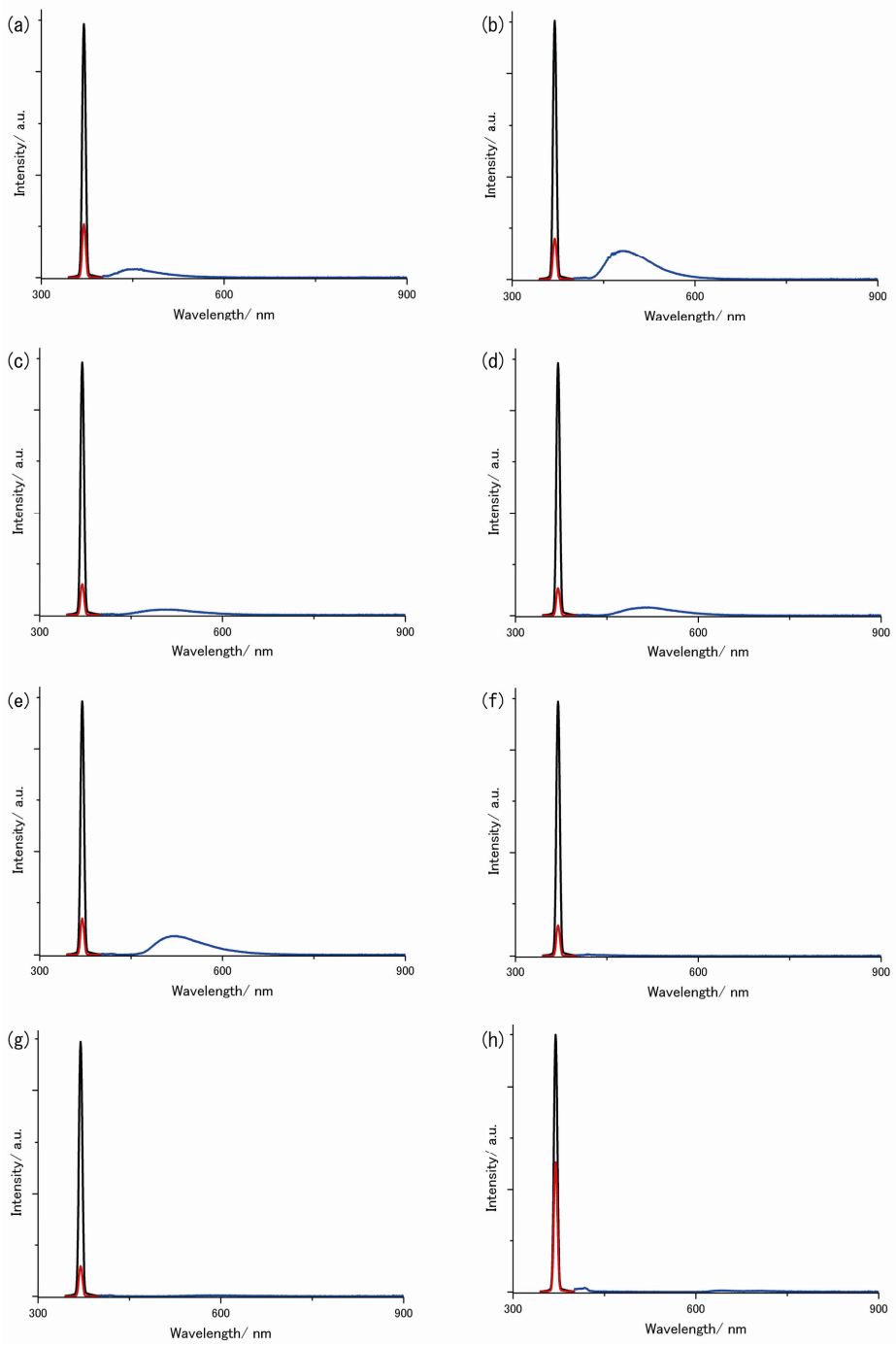
$$I_{flu}(t) = A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2) \quad + \ldots.$$

where A_i are the preexponential factors related with the statistical weights of each exponential and τ_1 are the lifetimes of each exponential decay (summarized in Supplementary Table S1). The goodness of the deconvolution process was controlled by the chi-squared (χ^2) and Durbin-Watson (D.W.) statistical parameters and the residual analysis.

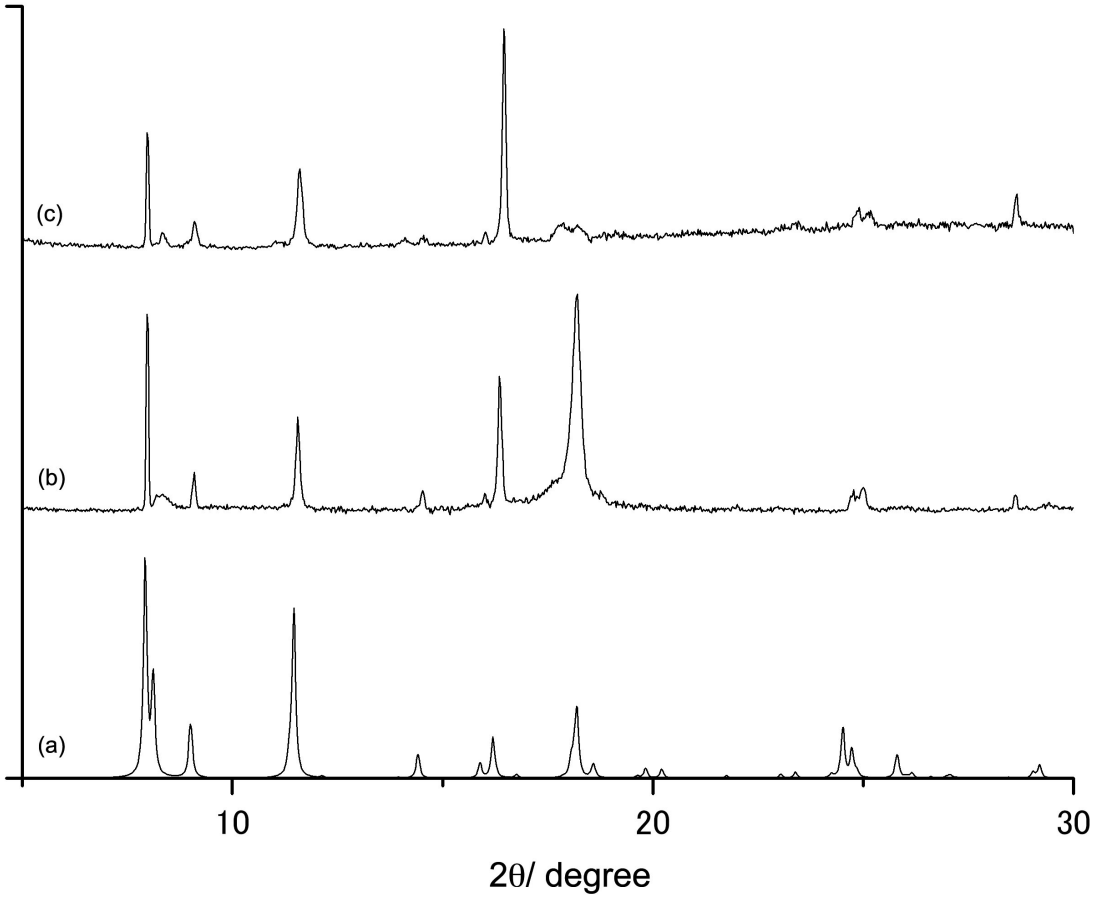
Generally, the decay curves were fit as 3-exponential and the intensity average lifetime for the samples was evaluated by means of :

$$\langle \tau \rangle_{ia} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

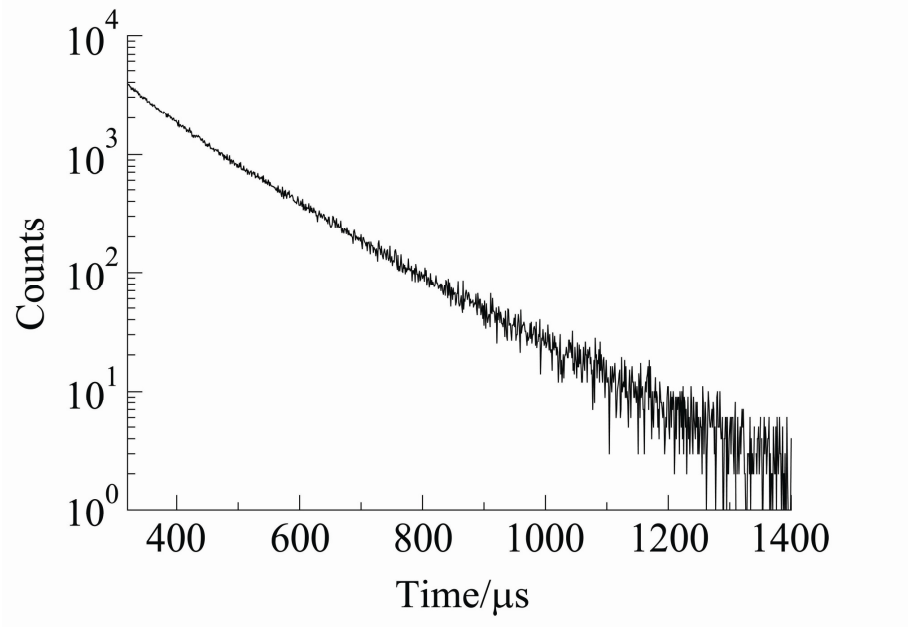
which represents the average time in which the molecules are in the excited state.[49]



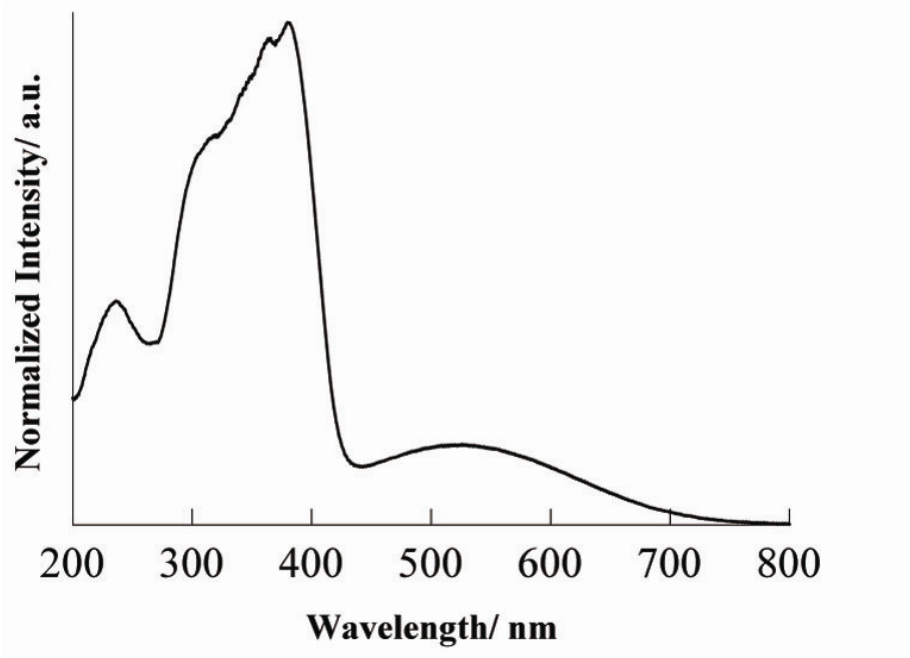
Supplementary Figure S10 | Quantum yield of **1⊃VOCs**. (VOCs: (a) benzene, (b) toluene, (c) *o*-xylene, (d) *m*-xylene, (e) *p*-xylene, (f) benzonitrile, (g) anisole and (h) iodobenzene) measured in the solid state at room temperature. Excitation wavelength is 370 nm. Black line: reflectance from Spectralon®, red line: reflectance from samples, blue line: emission spectra from the samples (the spectra were enlarged 10 times.)



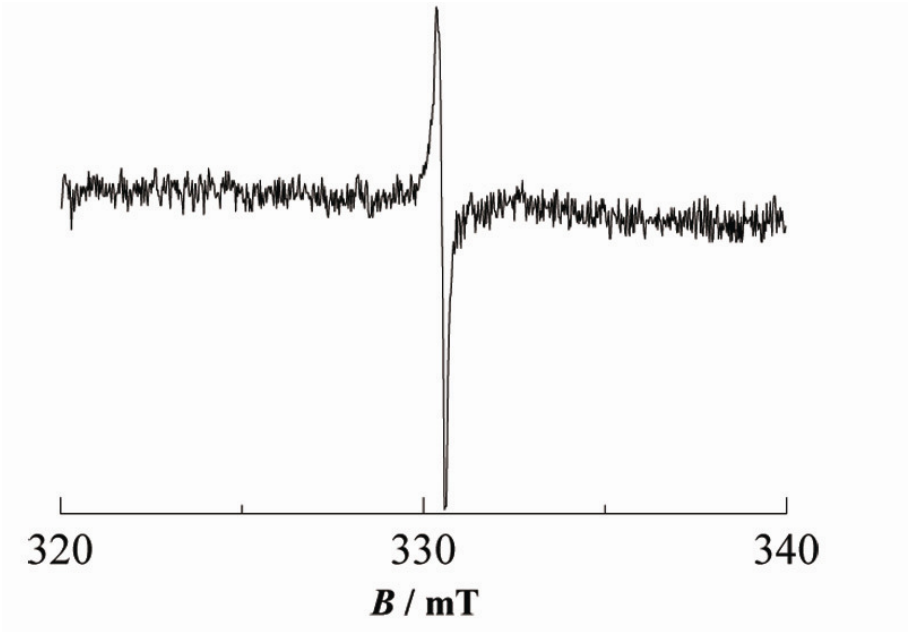
Supplementary Figure S11 I PXRD patterns of (a) simulated **1c** obtained from single crystal determination, (b) **1⊃NDMA**, and (c) **1⊃iodobenzene**, showing the **1c** type structure.



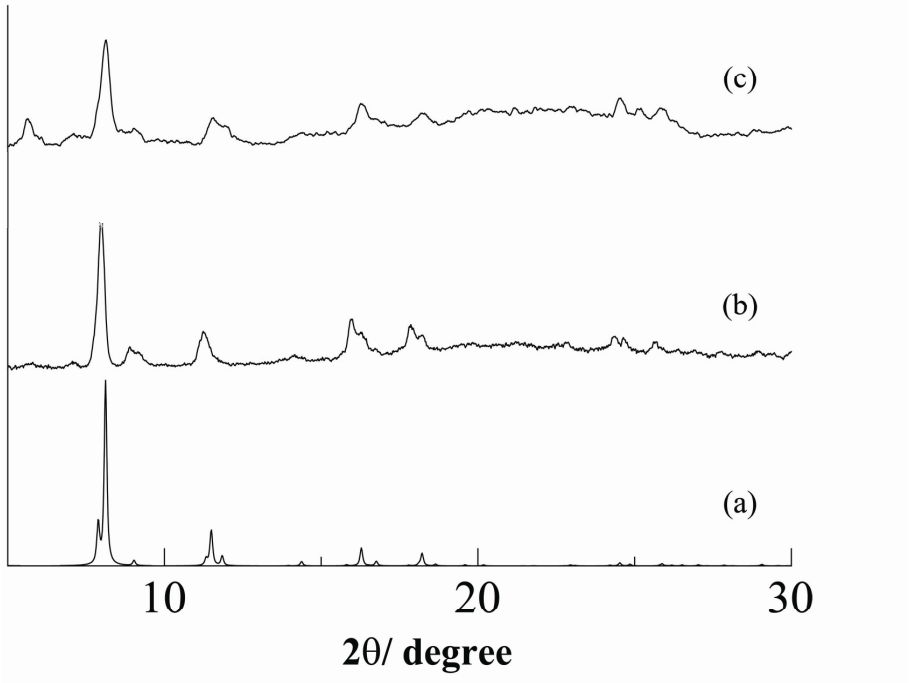
Supplementary Figure S12 | Phosphorescence decay curves of **1⊃iodobenzene**.



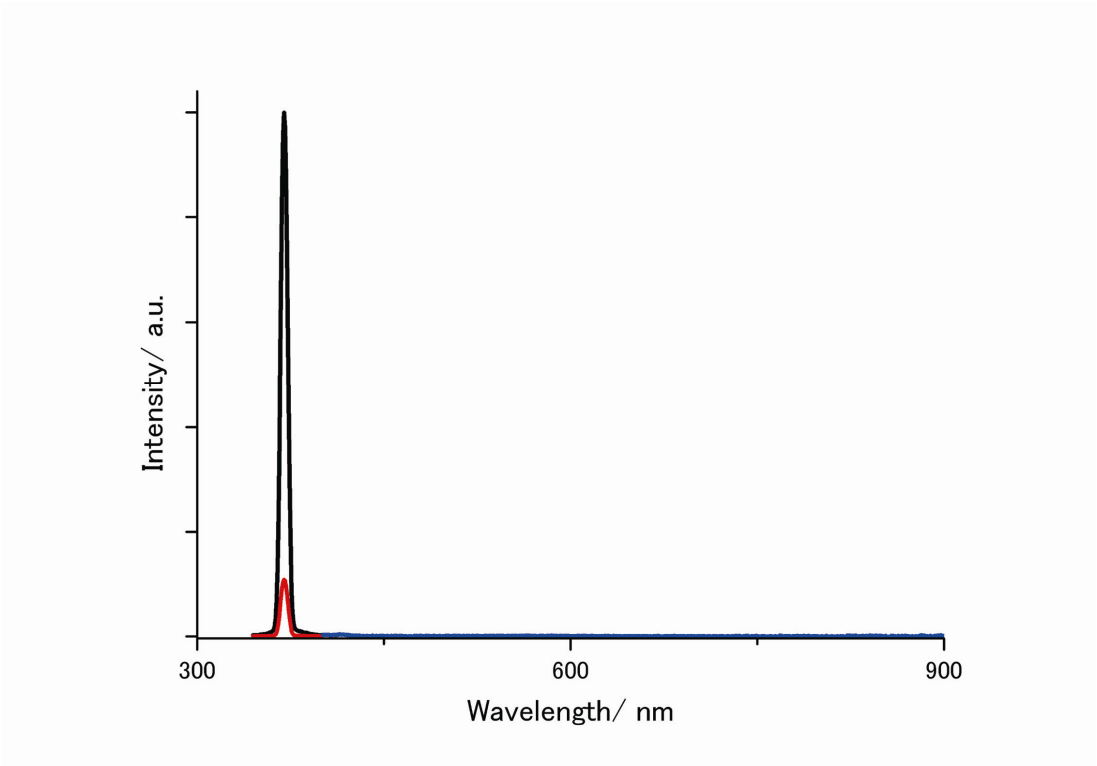
Supplementary Figure S13 | Diffuse reflectance UV-Vis spectrum of **1⊃NDMA**.



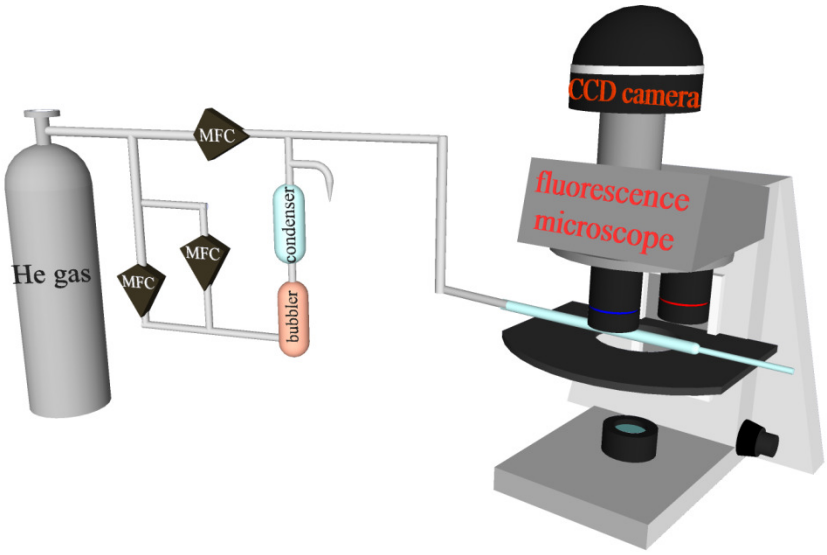
Supplementary Figure S14 | EPR spectrum of **1⊃NDMA** at 77K. g = 1.9944



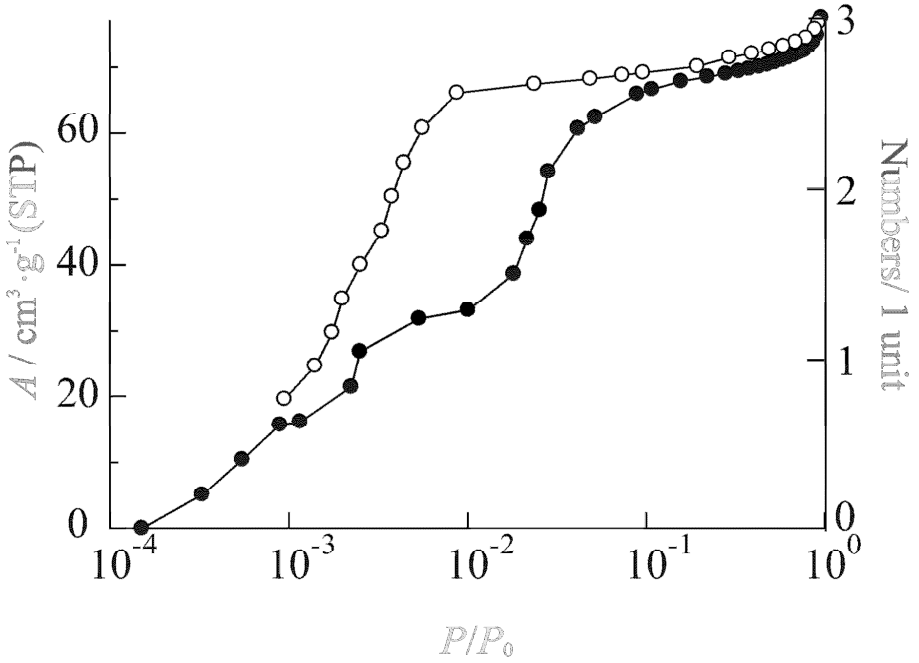
Supplementary Figure S15 I XRD patterns of (a) simulated $[Zn_2(ndc)_2(dpNDI)]_n$ from single crystal, (b) experimental as-synthesized form with DMF guest molecules, (c) Guest exchanged sample with toluene.



Supplementary Figure S16 | Quantum yield of $[Zn_2(ndc)_2(dpNDI)]_n$ with toluene as guest molecule measured in the solid state at room temperature. Excitation wavelength is 370 nm. Black line: reflectance from Spectralon®, red line: reflectance from samples, blue line: emission spectra from the samples (the spectra were enlarged 10 times.).



Supplementary Figure S17 | Experimental apparatus for fluorescent measurements under toluene vapor.



Supplementary Figure S18 I Adsorption (filled circle) and desorption (open circle) isotherms for benzene at 298K plotted against logarithmic relative pressure.

Guest	λ/nm	τ_1/ns (%A)	τ_2/ns (%A)	τ_3/ns (%A)	τ_{ia} (ns)
benzonitrile	420	0.1 (85%)	0.4 (15%)	-	0.2
benzene	450	0.7 (50%)	3.0 (45%)	12 (5%)	5
toluene	470	0.4 (18%)	6.0 (21%)	16.0 (61%)	14.8
o-xylene	500	1.8 (45%)	6.3 (45%)	23 (10%)	12.1
m-xylene	500	0.9 (25%)	7.5 (30%)	21.1 (45%)	18.2
p-xylene	520	1.5 (14%)	9.1 (28%)	25.6 (58%)	22.9
anisole	600	0.4 (2%)	3.6 (48%)	6.6 (50%)	5.6
I-benzene*	640				

Supplementary Table S1 I Summary of lifetime analyses for **1⊃VOCs**. Fluorescence lifetimes (τ) preexponetial factor in percentage (%A). λ = emission wavelength of registration after excitation at 370 nm and τ_{ia} intensity average lifetime.

λ/nm	τ_1 /μs (%A)	τ_2 /μs (%A)	τ_{ia} (μs)
640	66.8 (20.3%)	147 (79.7%)	139

Supplementary Table S2 | Lifetime analysis for **1⊃iodobenzene**. Phosphorescence lifetimes (τ) preexponetial factor in percentage (%A). λ = emission wavelength of registration after excitation at 370 nm and τ_{ia} intensity average lifetime.

Supplementary References

49. Lakowicz, J.R. *Principles of Fluorescence Spectroscopy,* 2ª Ed., Kluwer Academic, New York, 1999