Electronic Supplementary Material (ESI) for CrystEngComm
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Vapor Phase Detection of Nitroaromatic and Nitroaliphatic Explosives by Fluorescence Active Metal Organic Frameworks

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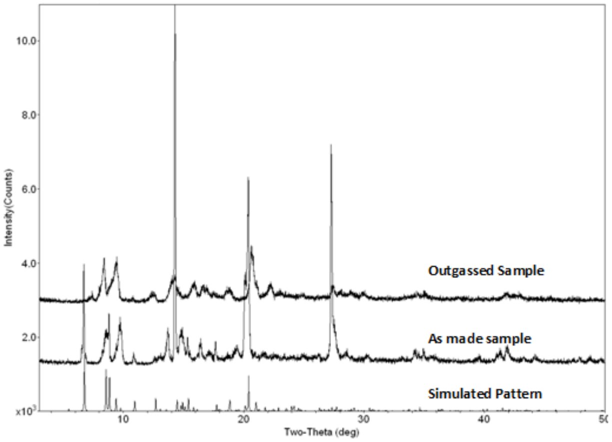
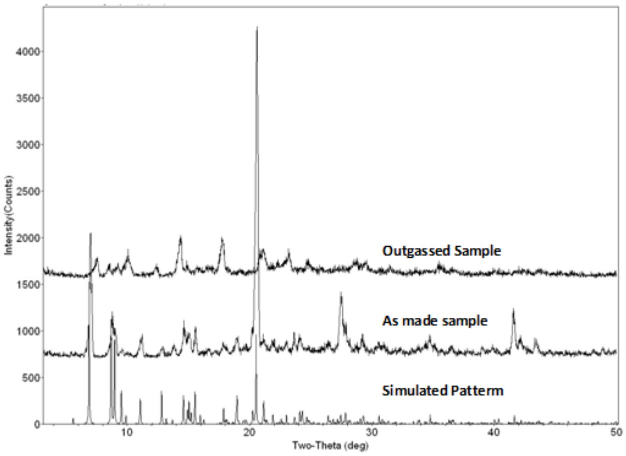
Supporting Information

S1. Powder X-ray Diffraction (PXRD) and Thermogravimetric Analysis (TGA)

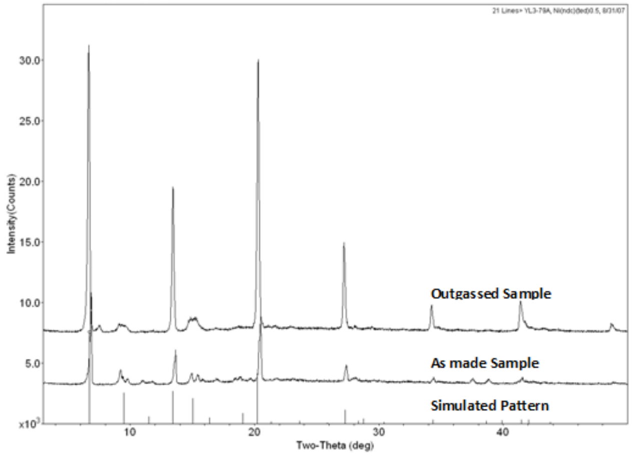
Powder X-ray diffraction experiments for compounds **1**-**3** were conducted using a D/M-2200T automated system with Cu Kα radiation (λ=1.5406 Å). The graphite monochromatic was used and the generator power settings were at 40 kV and 40 mA. Powder X-ray diffraction for compound **4** was collected in a Rigaku Ultima-IV diffractometer with Cu Kα radiation (λ = 1.5406 Å) between 2θ of 5° - 40° at a power setting of 40 kV and 44 mA. The thermal properties of the compounds **1**-**3** were evaluated using a TA Instruments Q50 TG unit. The samples (~10 mg) were loaded onto a sample pan and heated from room temperature to 600 °C at a rate of 10 °C/min under N_2 (flow and purge rate at 40 mL/min and 60 mL/min, respectively). The thermal property of compound **4** was measured in a Q5000 TG unit under similar experimental condition.



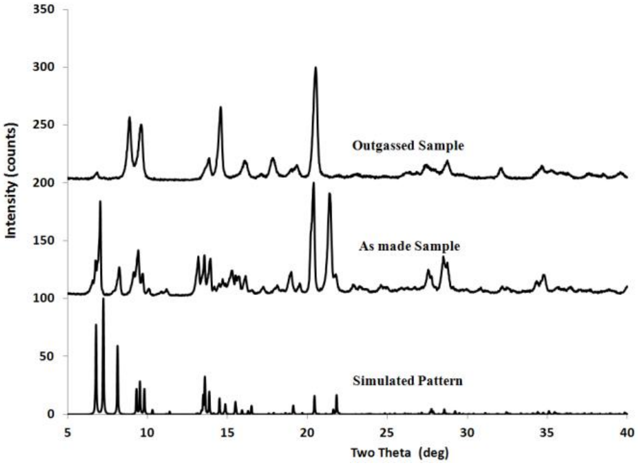
(a)



(b)

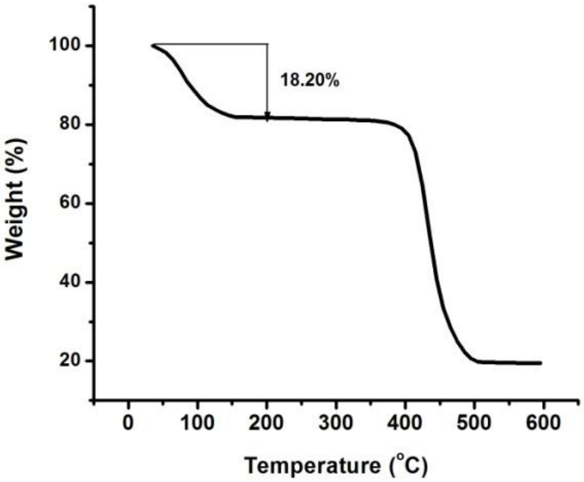


(c)

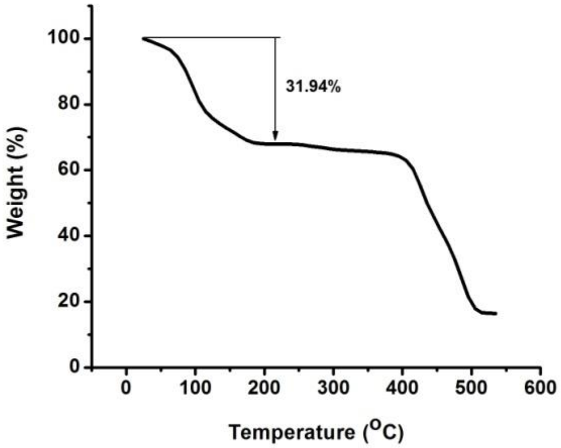


(d)

Figure S1. Powder X-ray diffraction patterns of as made and outgassed sample of compounds **1** (a), **2** (b), **3** (c) and **4** (d), respectively, along with simulated patterns.


18.20%
Weight (%)
100
80
60
40
20
0
100
200
300
400
500
600
Temperature (°C)

(a)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Weight (%)
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0
100
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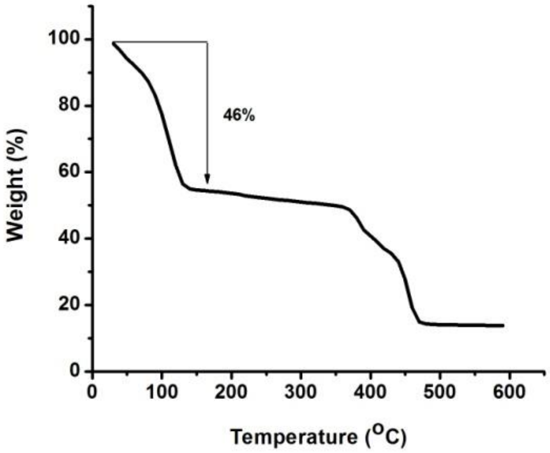
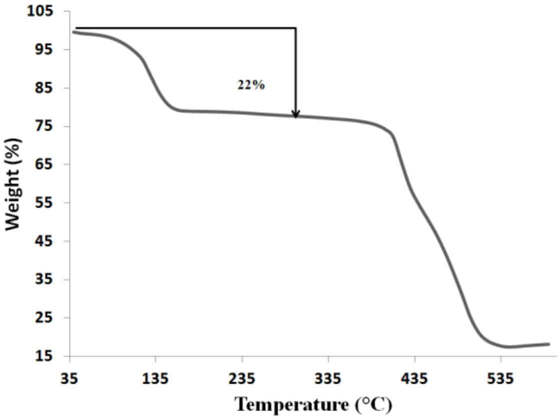
500
600
Temperature (°C)

(b)


46%
Weight (%)
100
80
60
40
20
0
0
100
200
300
400
500
600
Temperature (°C)

(c)

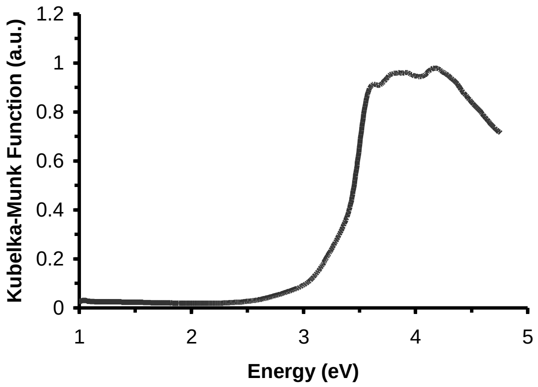


(d)

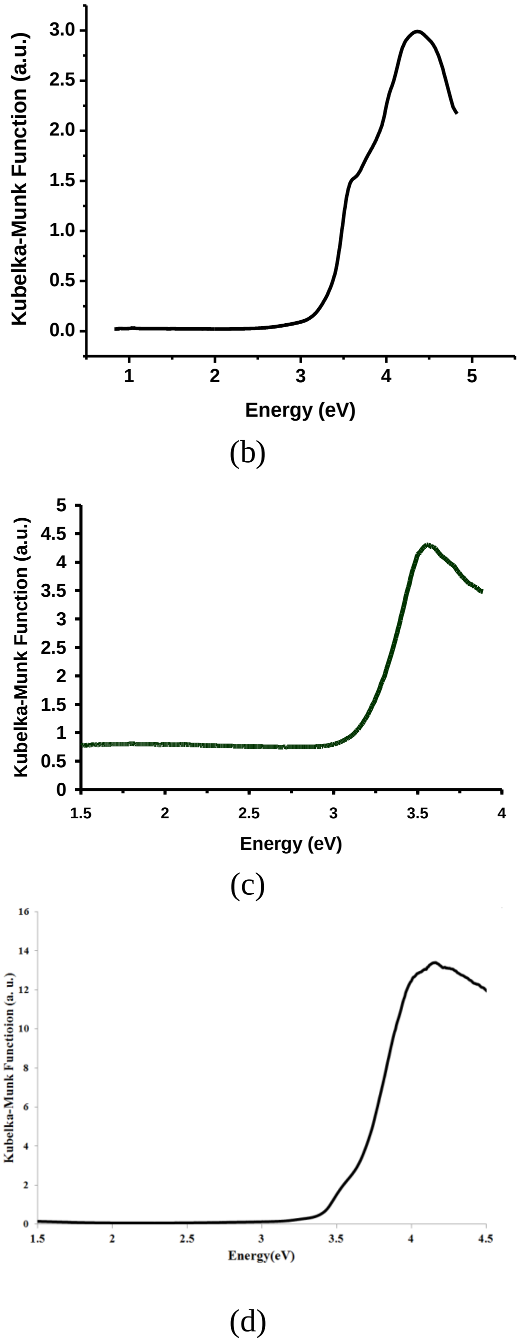
Figure S2. Thermogravimetric (TG) profiles of compounds **1** (a), **2** (b), **3** (c) and **4** (d) respectively.

S2. Optical Measurements

The optical absorption spectra of all outgassed FAM samples (in powder form) were collected on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. The room temperature diffuse reflectance of FAM samples was measured and converted to Kubelka-Munk Function, from which the band gap of each compound was estimated.



(a)



(b)

(c)

(d)

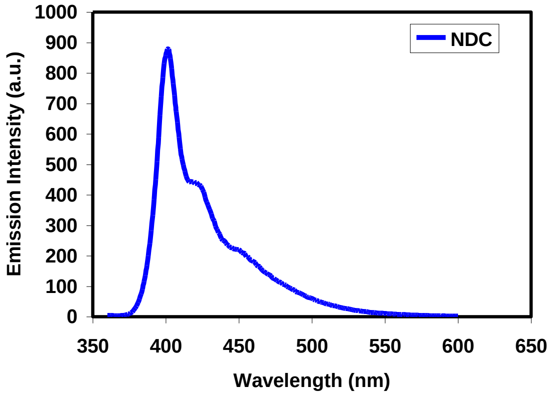
Figure S3. The optical absorption spectra of solid samples of **1′-4′**. Their optical band gaps are estimated to be ~3.4, ~3.3, ~3.1 and 3.5 eV, respectively.

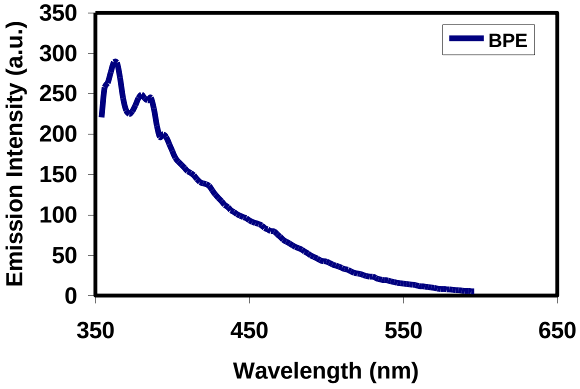
S3. Thin-Layer Sample Preparation and Photoluminescence Measurements

A glass slide (~ 16 × 60 mm) was rinsed with distilled water and ethanol. Scotch (black) tape was then applied to the lower half of the slide. The tape was peeled off from the slide after few minutes, so that the glue from the tape was stuck on the glass slide. Ground powder of the as-made (or outgassed) sample was then sprinkled evenly onto the glued surface of the slide. The extra samples were removed by gentle tapping and putting the face of the slide down. By this process a very thin layer of sample was formed on the glass surface.

All nitro-explosives and other aromatic and aliphatic compounds included in this work were purchased commercially and used as received. For solid analytes (m-DNB, p-DNB, DNT and DMNB), 1 g of each was placed in small (20 mL) open glass vials and these vials were placed into capped (500 mL) glass bottles for several days to ensure that the equilibrated vapor pressure of each analyte was reached. For the liquid sample (NB, NT, BZ, TO and ClBZ), 1 mL of each was taken and the same procedure was followed.

Fluorescence spectra of thin-layer samples of FAMs were collected before the exposure to a selected analyte. The sample was then placed in the large glass bottle for a designated time period. After specified exposure time, the slide was taken out and mounted to the sample holder of the fluorescence spectrophotometer. Emission spectrum was recorded immediately. For comparison purposes, PL spectra were also collected on all ligands.





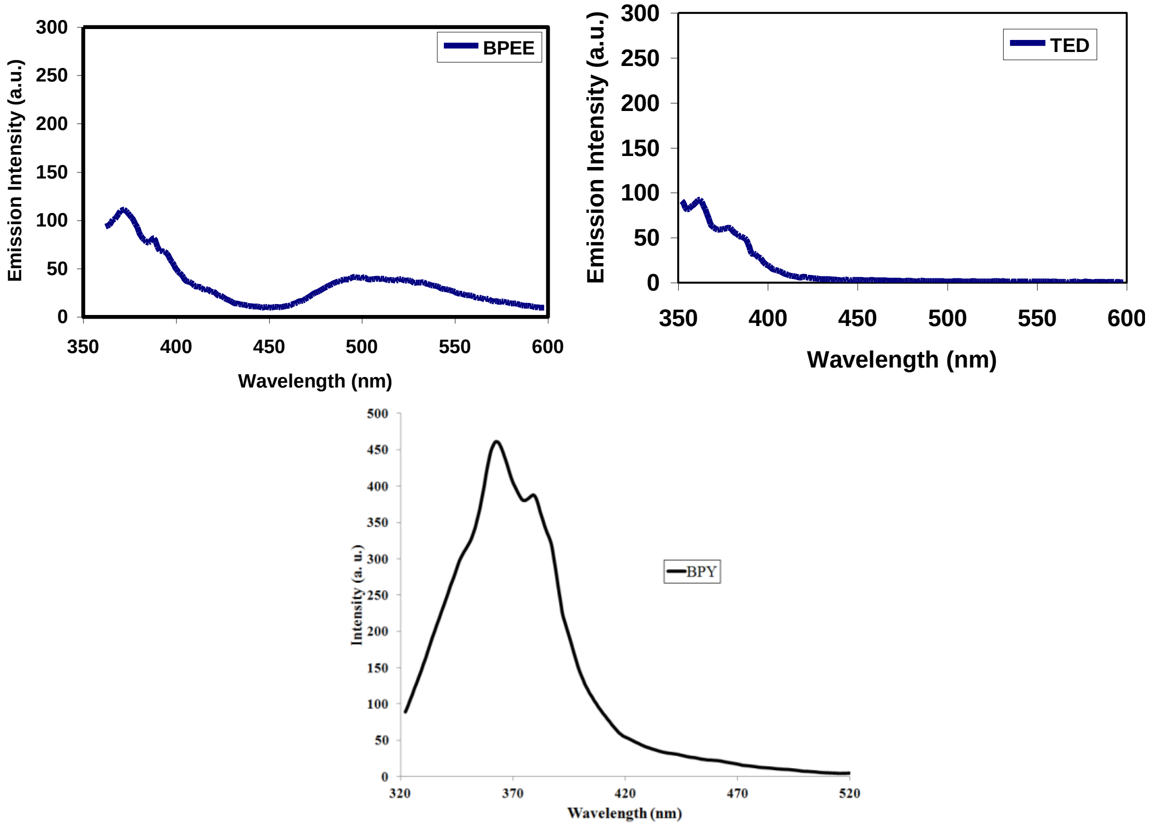
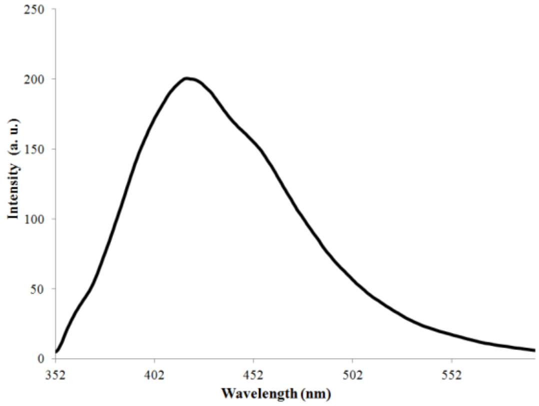
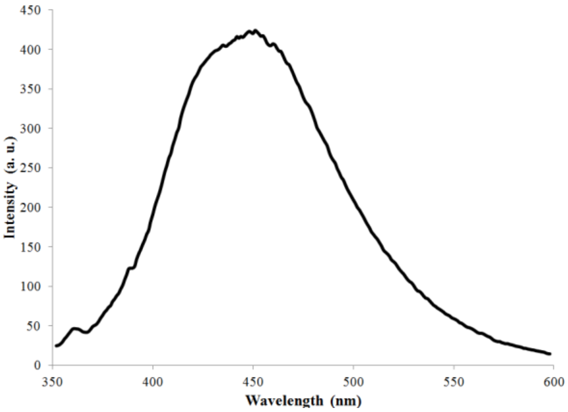


Figure S4. Emission spectra of thin-layer samples of ndc (λ_{ex}: 340 nm), bpe, bpee, ted (λ_{ex}: 330 nm) and bpy (λ_{ex}: 300 nm). The emission spectra of all five ligands show very little dependence on the excitation wavelength between 330 and 350 nm.



(a)



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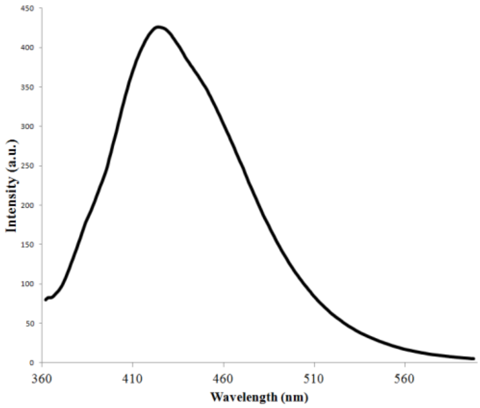

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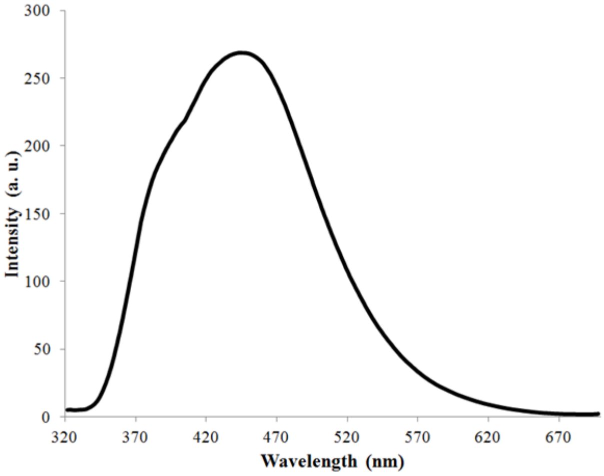

(d)

Figure S5. Emission spectra of thin-layer samples of (a) **1**$^{'}$ (λ_{ex}: 330 nm), (b) **2**$^{'}$ (λ_{ex}: 330 nm, (c) **3**$^{'}$ (λ_{ex}: 340 nm) and (d) **4**$^{'}$ (λ_{ex}: 300 nm).

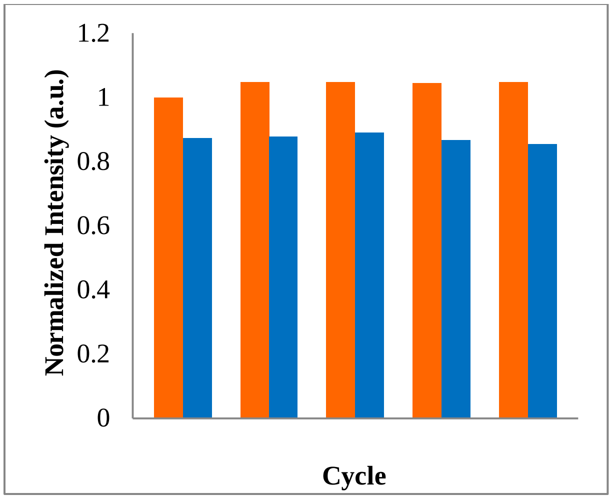

Figure S6. Recyclability test on **1'**. Nitromethane was used as a model analyte. Analyte vapor exposure time was 5 minutes. Fluorescence can be regenerated by heating the sample at 120 °C for 2 minutes. 5 consecutive cycles of quenching were achieved. Orange bar: emission of outgassed sample. Blue bar: emission after exposure to nitromethane for 5 minutes.

S4. Electrochemical Measurement

Electrochemical measurements of all FAMs were carried out at room temperature in a three-electrode cell (Figure S7). An AFCBP1 bipotentiostat connected to a rotating ring-disk electrode was used in the electrochemical measurement. A glassy carbon (GC) rod (diameter 3 mm, geometric area 0.071 cm^2, Pine Research Inst) was implanted in polyether ether ketone (PEEK) and was coated with the FAMs as follows: 50 mg of each FAM sample was ultrasonicated in ethanol (5 mL) until a nice dispersion was achieved. Then, 100 μL of the suspension was transferred quantitatively onto the GC electrode, which had been previously polished. The electrode was dried at room temperature until the solvent disappeared and thin film of FAMs was formed on the top of GC electrode. The GC electrode coated with the FAM sample was used as the working electrode, and a platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrochemical measurements of the analytes were done by dissolving 0.01 mM analytes in electrolyte composed of 25% acetone and 75% 0.1 M LiCl in water or 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) in acetonitrile. In case of analytes, the GC electrode was also used as the working electrode, and a platinum wire and SCE were used as the counter and reference electrodes, respectively. The electrochemical behavior of all four compounds and analytes were evaluated by cyclic voltammetry. To make the results comparable, cyclic voltammograms of ferrocene were recorded in both electrolytes as internal standard and corrections in the data were made if needed.

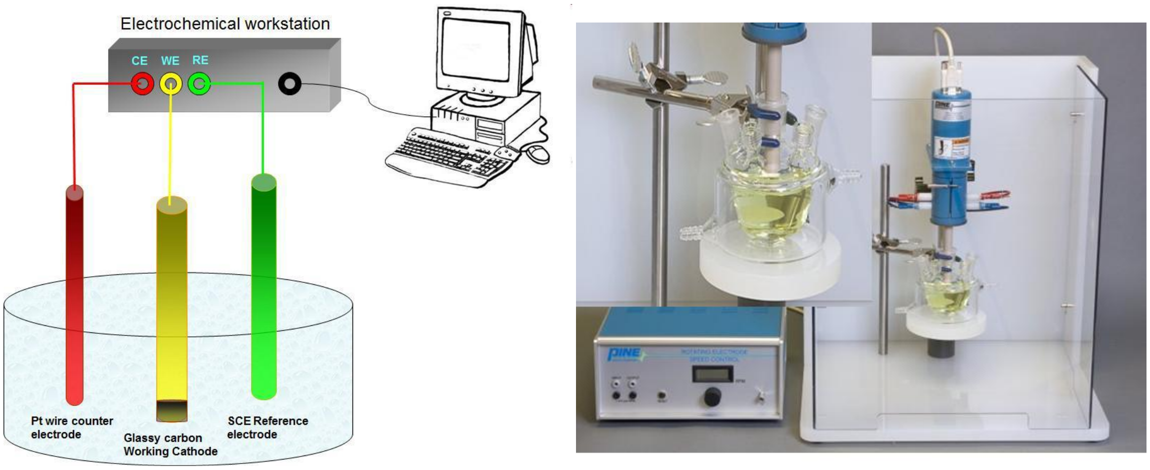

Figure S7. Schematic (left) and actual experimental (right) set-up for electrochemical measurements.

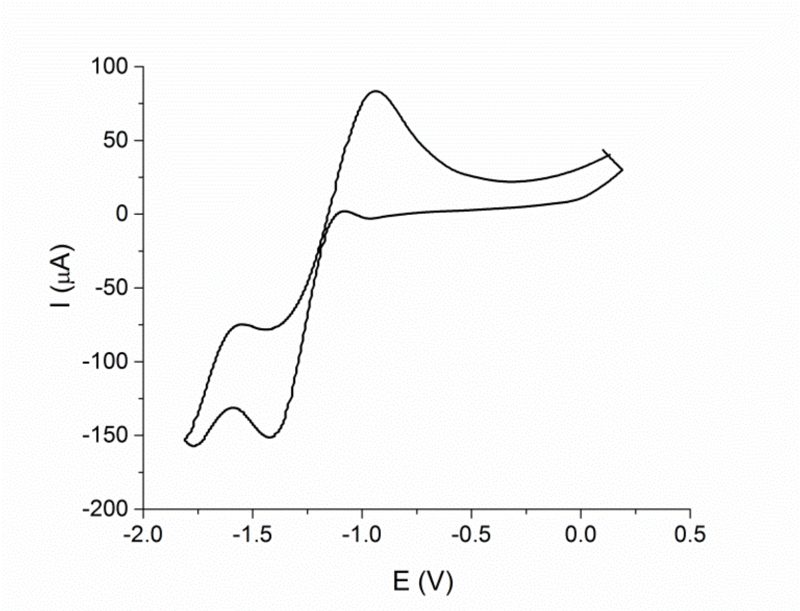

Figure S8. The CV curve of **1** measured in 0.1M LiCl in water/acetone (v/v = 3:1). The reduction potential is -1.2V after correction with the internal standard Ferrocene.

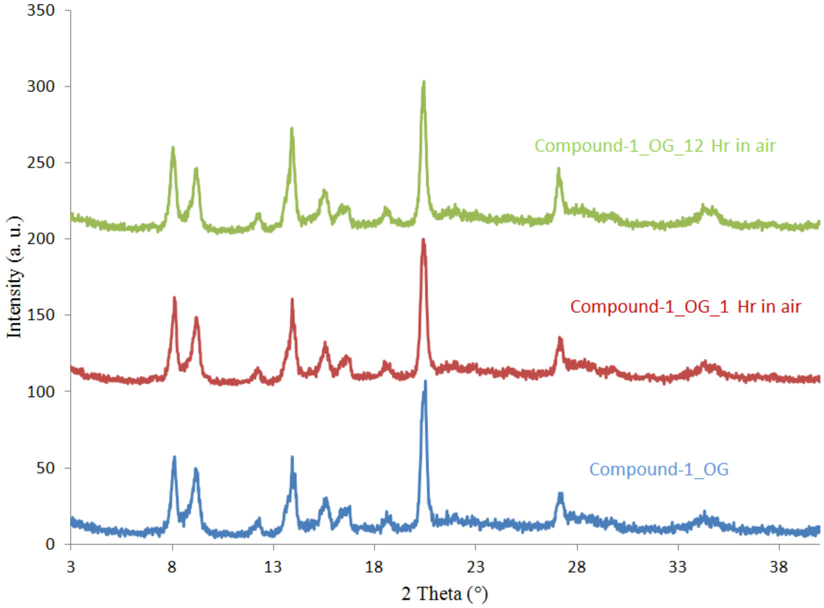

Figure S9. Stability of compound **1’** in air as observed by PXRD. Blue: PXRD pattern of activated sample **1**’. Red: PXRD pattern of **1’** after 1 hour exposure in air. Green: PXRD pattern of **1**’ after 12 hours exposure in air.

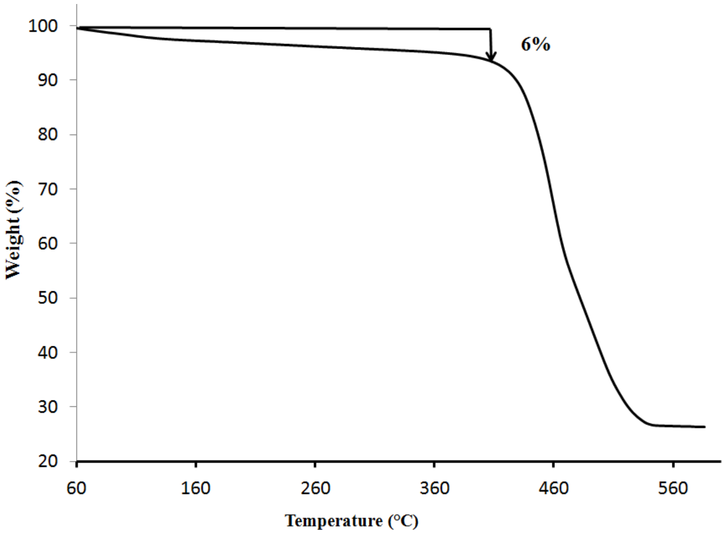

Figure S10. Observed weight loss for compound **1'** after exposure to TO vapor for 10 minutes.

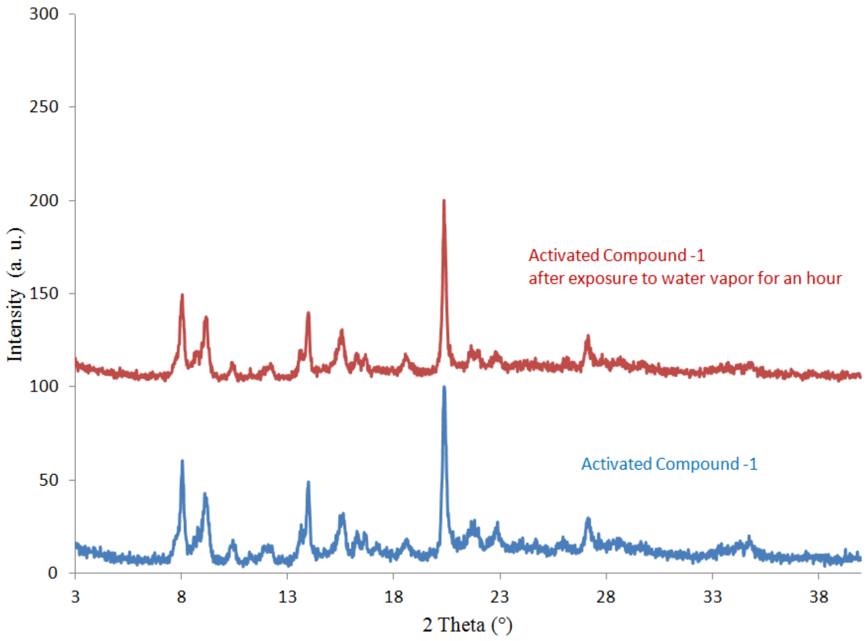

Figure S11. The stability of compound **1'** in water vapor. Blue: PXRD of active sample **1**'. Red: PXRD of active **1**' after 1 hour exposure to saturated water vapor at room temperature.

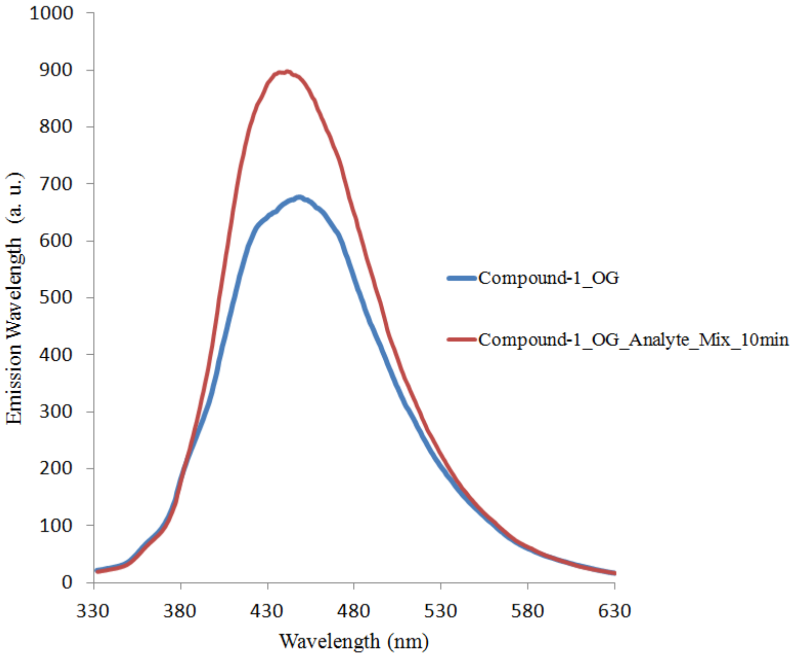

Figure S12. The effect of analytes mixture (BZ and NM (v/v) 1:1) on compound **1'** (10 minutes exposure). Blue: initial PL emission spectrum of active sample **1**'. Red: PL emission spectrum of **1**' after 10 minutes exposure to analytes mixture at room temperature.

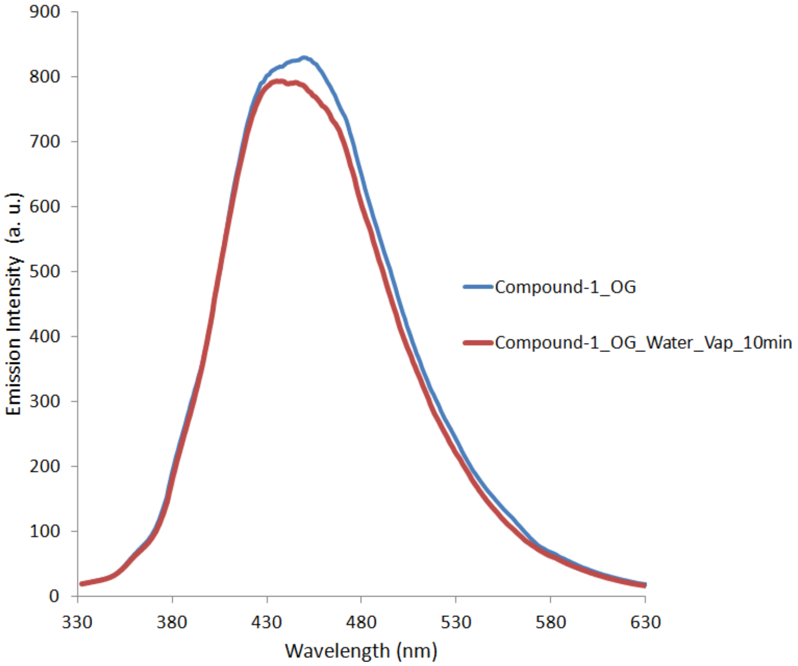

Figure S13. The effect of water vapor on the PL properties of compound **1**'. Blue: initial PL emission spectrum of activated sample **1’**. Red: PL emission spectrum of **1**’ after 10 minutes exposure to air and saturated water vapor at room temperature.