Supporting Information

On/Off Luminescence Vapochromic Sensing of Benzene and Its Methylated Derivatives by a Trinuclear Silver(I) Pyrazolate Sensor

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Experimental Section

Spectroscopic Measurements. Steady-state photoluminescence spectra were acquired with a PTI QuantaMaster Model QM-3/2006SE scanning spectrofluorometer equipped with a 75-watt xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. The emission spectra were corrected for the detector wavelength-dependent response. The excitation spectra were also corrected for the wavelength-dependent lamp intensity. Temperature-dependent studies were acquired with an Oxford optical cryostat using liquid nitrogen as coolant. Lifetime data were acquired using a high speed pulsed xenon lamp source interfaced to the PTI instrument along with an autocalibrated "QuadraScopic" monochromator for excitation wavelength selection. Table S1 and Figures S1-S5 show additional luminescence spectral data in addition to the ones shown in the main manuscript.

SAM Uptake and Loss Measurements. Thermogravimetric analysis (TGA) was performed utilizing a TA Instruments Q50 TGA analyzer for dry and SAM-exposed samples of $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ (**1**) . The weight change was monitored upon ramping the temperature at a rate of 20.00 °C/min up to 900 °C. Adsorption and desorption isotherms were obtained via a TA Instruments Q5000 SA dynamic vapor sorption analyzer for dry powder samples of **1**. These isotherms were measured at 25 °C by monitoring the weight change of the sample as a function of pressure of the solvent vapor relative to that of N_2

carrier gas for a known weight of **1** (~10-15 mg). The adsorbate was added incrementally. Data points were recorded at equilibrium, when no further weight change was observed (< 0.0100 wt % in 5 min with a maximum equilibrium time of 180 min). Figures S6-S9 show additional vapor uptake data in addition to the ones shown in the main manuscript.

Thin-Film X-Ray Diffraction Measurements. Drop-cast thin films of dry samples of **1** were prepared on glass slides. The glass slides were placed on a hot plate (65°C) and allowed to dry. The non-luminescent films were characterized with XRD. The films were then exposed to benzene vapor from a beaker for 25 minutes. After the thin film was exposed to benzene vapor luminescence was tested with a UV lamp. Luminescence was tested and ascertained to persist before and after the XRD scan. The sample was then placed on a hotplate at 65 °C for 30 minutes. After the sample was dry, it became non-luminescent when exposed to a UV lamp and was then characterized again with XRD.

Syntheses. Complex **1** was prepared based on the literature method (Dias, H. V. R.; Polacha, S. A.; Wang, Z. *J. Fluorine Chem.* **2000**, *103*, 163) with modification to dry the product using vacuum at room temperature overnight to remove the benzene solvent. The crystalline adducts of **1** with SAM molecules were prepared according to literature methods (Dias, H. V. R.; Palehepitiya Gamage, C. S. *Angew. Chem. Int. Ed.* **2007**, *46*, 2192; Krishantha, D. M. M.; Palehepitiya Gamage, C. S.; Schelly, Z. A.; Dias, H. V. R. *Inorg. Chem.* **2008**, *47*, 7065) and ascertained to have the same crystal form as the one reported by means of single crystal X-ray diffraction before examining the luminescence behavior of each binary adduct.

Table S1. Luminescence vapochromism test for a drop-cast thin film of **1** upon exposure to vapors of various solvents.

Vapor	Observation
Benzene	Bright green luminescence
Toluene	Bright green luminescence
Mesitylene	Bright blue luminescence
Chlorobenzene	No luminescence
Hexafluorobenzene	No luminescence
Acetone	No luminescence
Cyclohexanone	No luminescence
Acetophenone	No luminescence
Acetyl acetone	No luminescence
2,3-Butanedione	No luminescence
Benzaldehyde	No luminescence
Propionaldehyde	No luminescence
Tetrahydrofuran (THF)	No luminescence
Diethyl ether	No luminescence
Ethanol	No luminescence
Methanol	No luminescence
Dichloromethane	No luminescence
1,2-Dichloroethane	No luminescence
Chloroform	No luminescence
Hexane	No luminescence
Cyclohexane	No luminescence

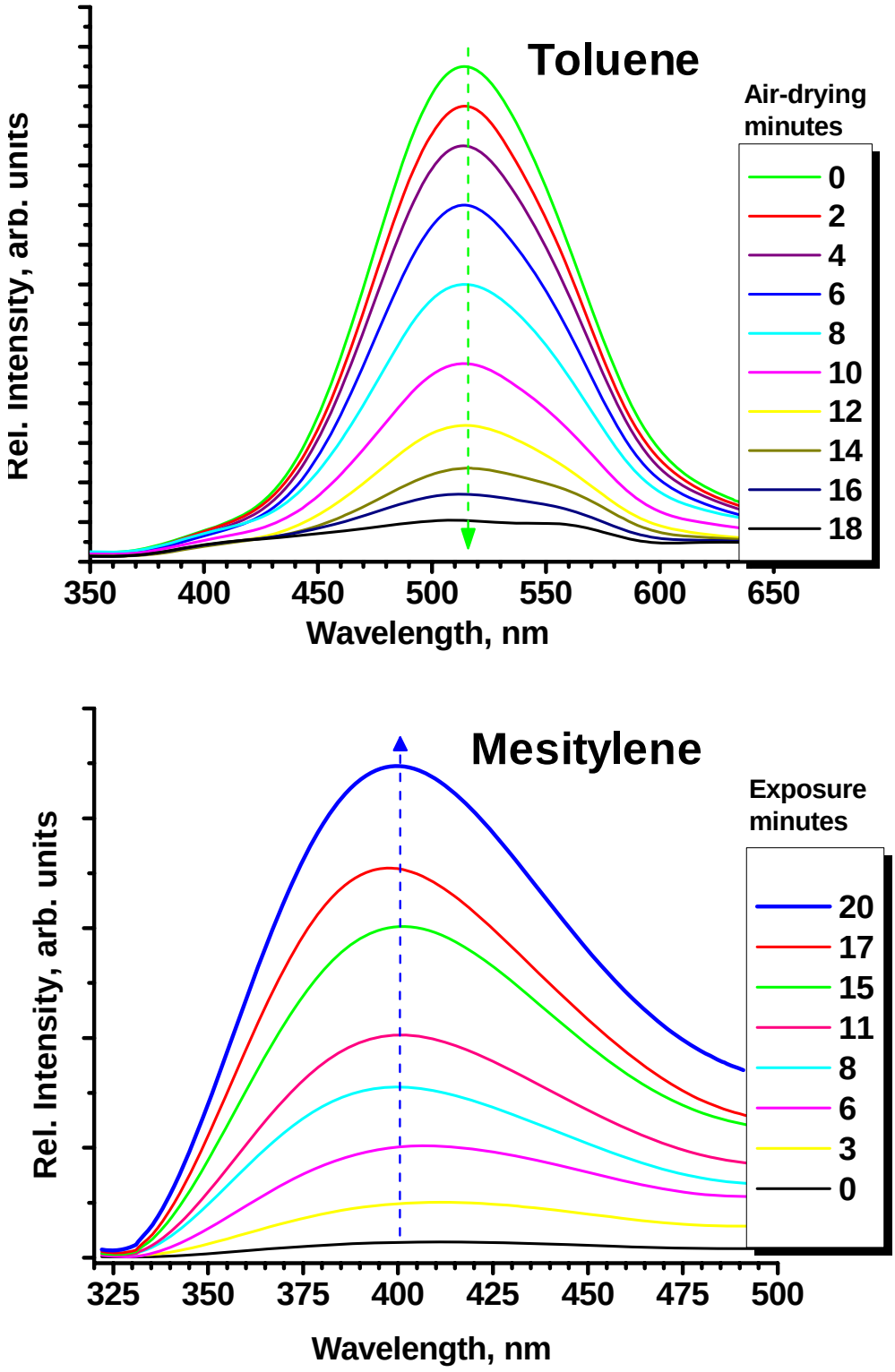

Figure S1. Luminescence vapochromism of a dry film of **1** showing disappearance of the green emission upon interaction with toluene vapor (top) and generation of the blue emission upon interaction with mesitylene vapor (bottom) at RT. The reverse processes are shown in the main manuscript (Figs. 1b-c).

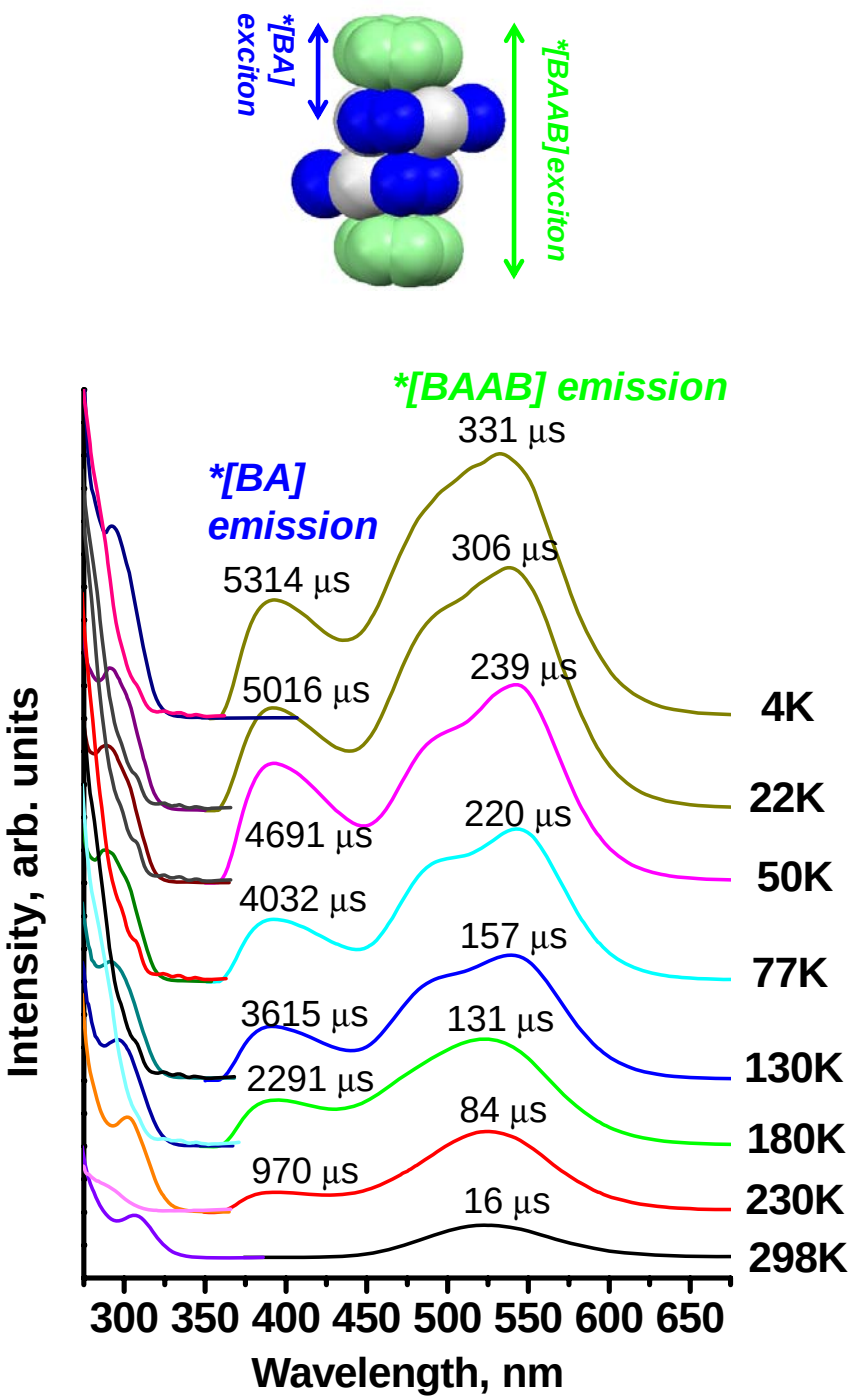

Figure S2. Photoluminescence spectra and lifetimes for single crystals of the binary adduct of **1** with benzene, [benzene·[**1**]$_2$·benzene], as a function of temperature.

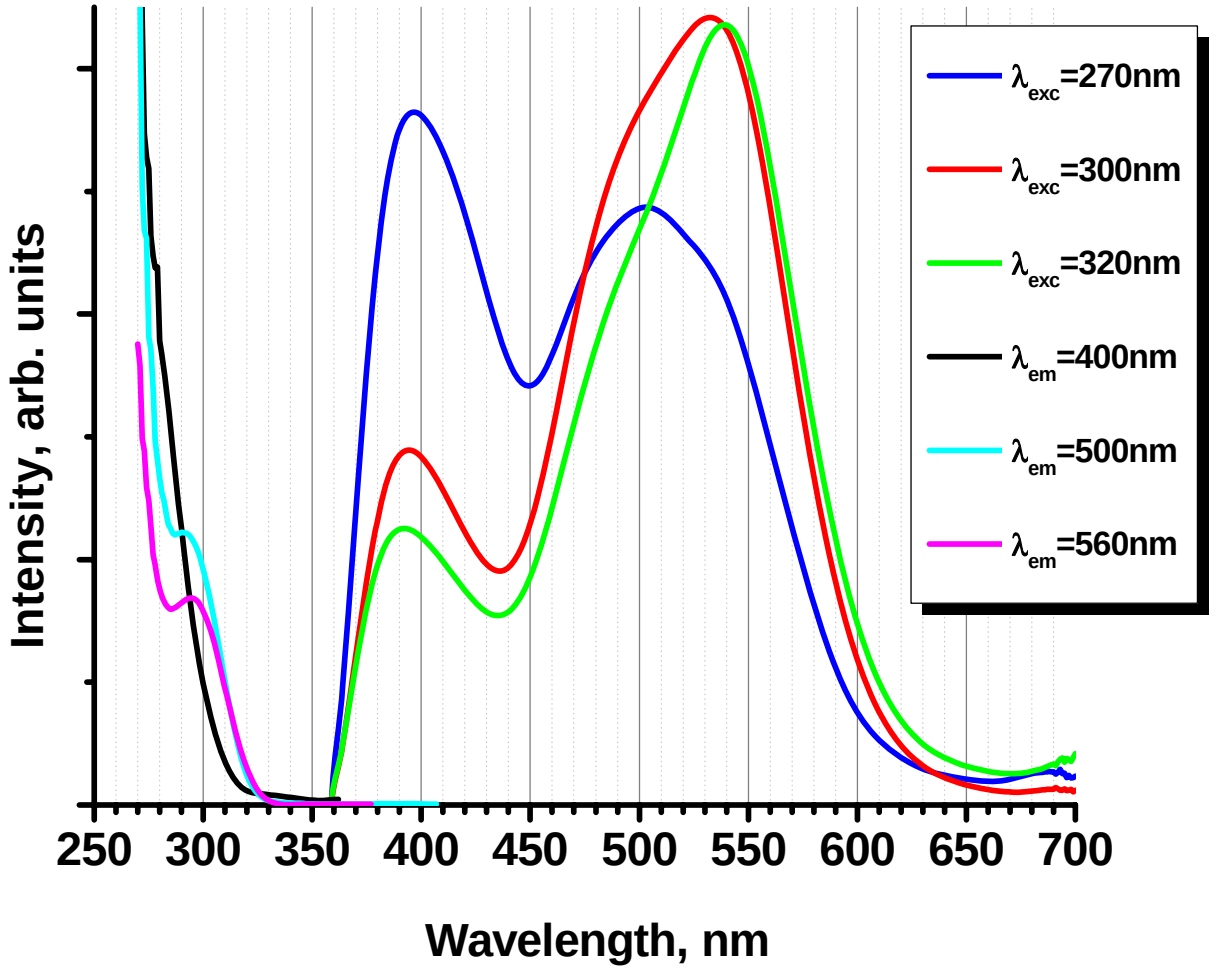

Figure S3. Photoluminescence spectra for single crystals of the binary adduct of **1** with benzene, [benzene·[**1**]$_2$·benzene], at 4 K using different excitation and emission wavelengths.

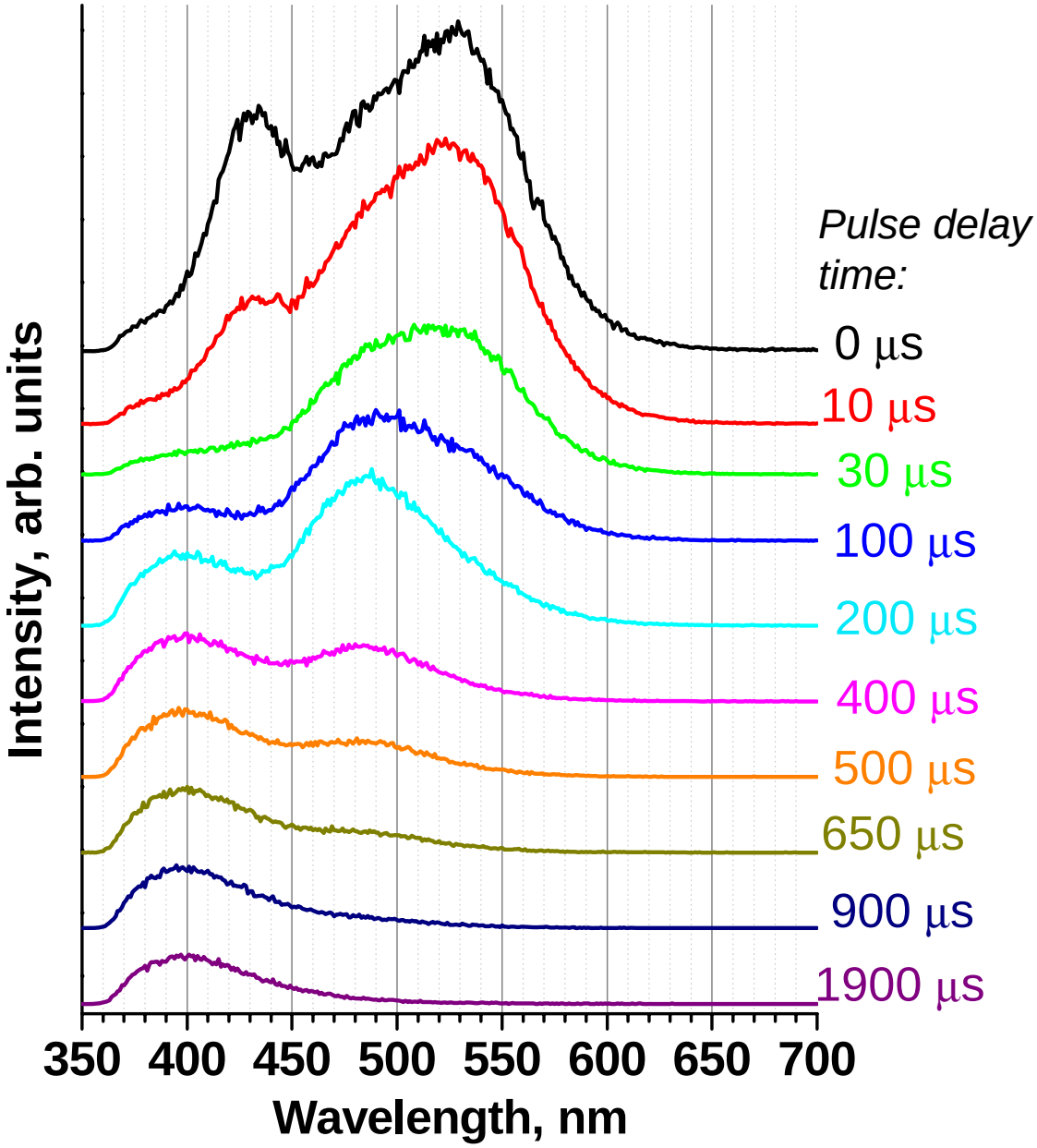

Figure S4. Time-resolved photoluminescence spectra for single crystals of the binary adduct of **1** with benzene, [benzene·[**1**]$_2$·benzene], at 4 K using different delay times following the laser pulse.

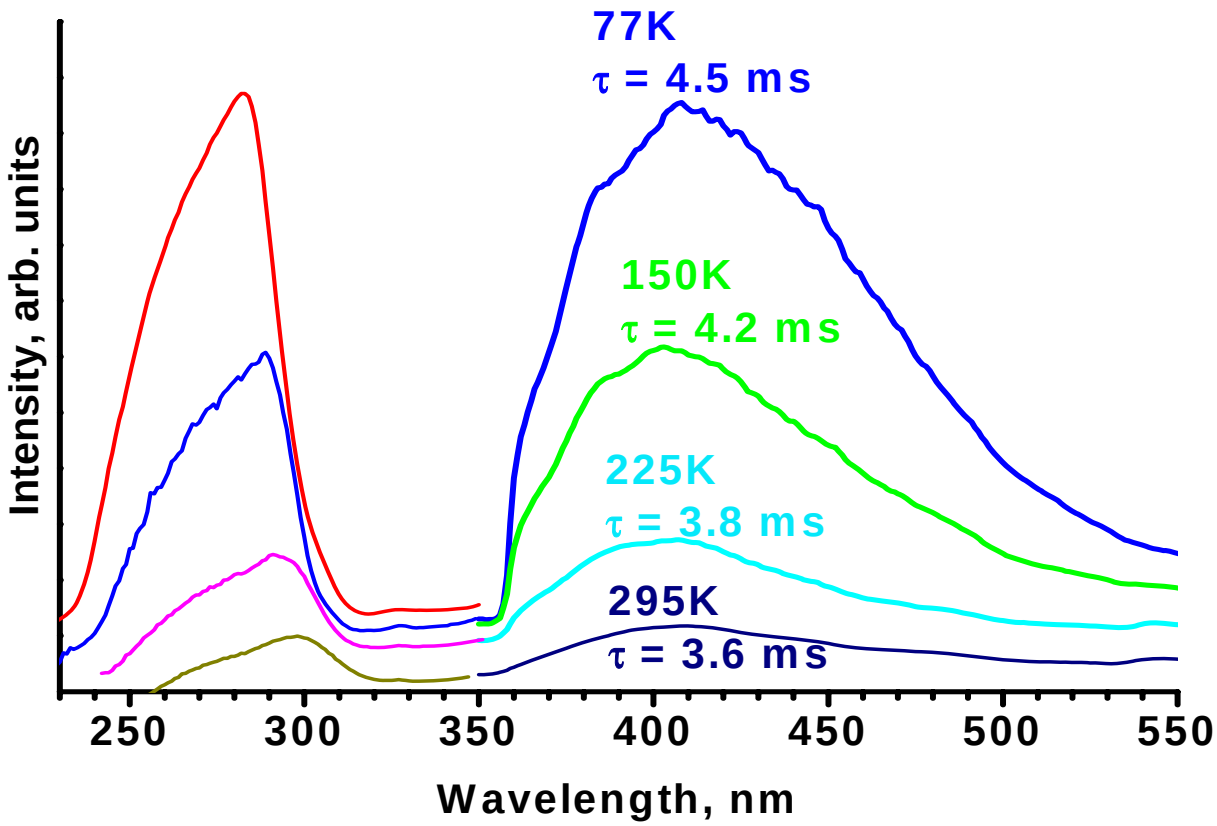

Figure S5. Photoluminescence spectra and lifetimes for single crystals of the binary adduct of **1** with mesitylene, {**1**·mesitylene}$_\infty$, as a function of temperature.

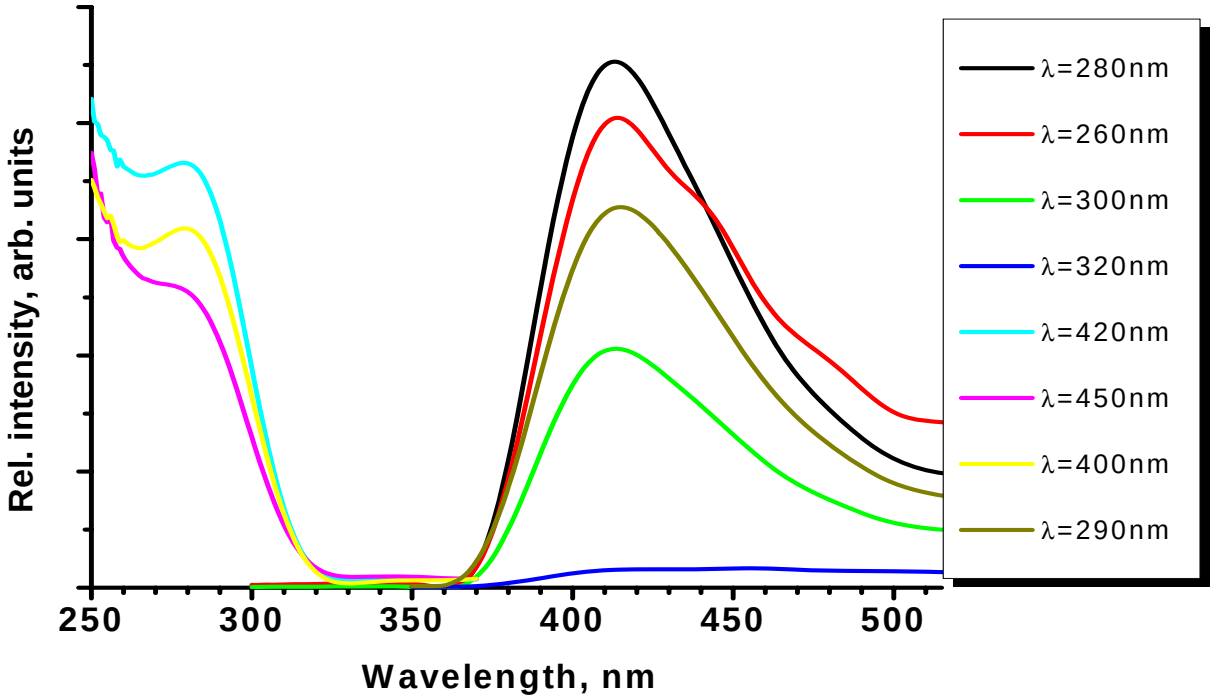

Figure S6. Photoluminescence spectra for a solid film of **1** exposed to mesitylene vapor at room temperature using different excitation and emission wavelengths.

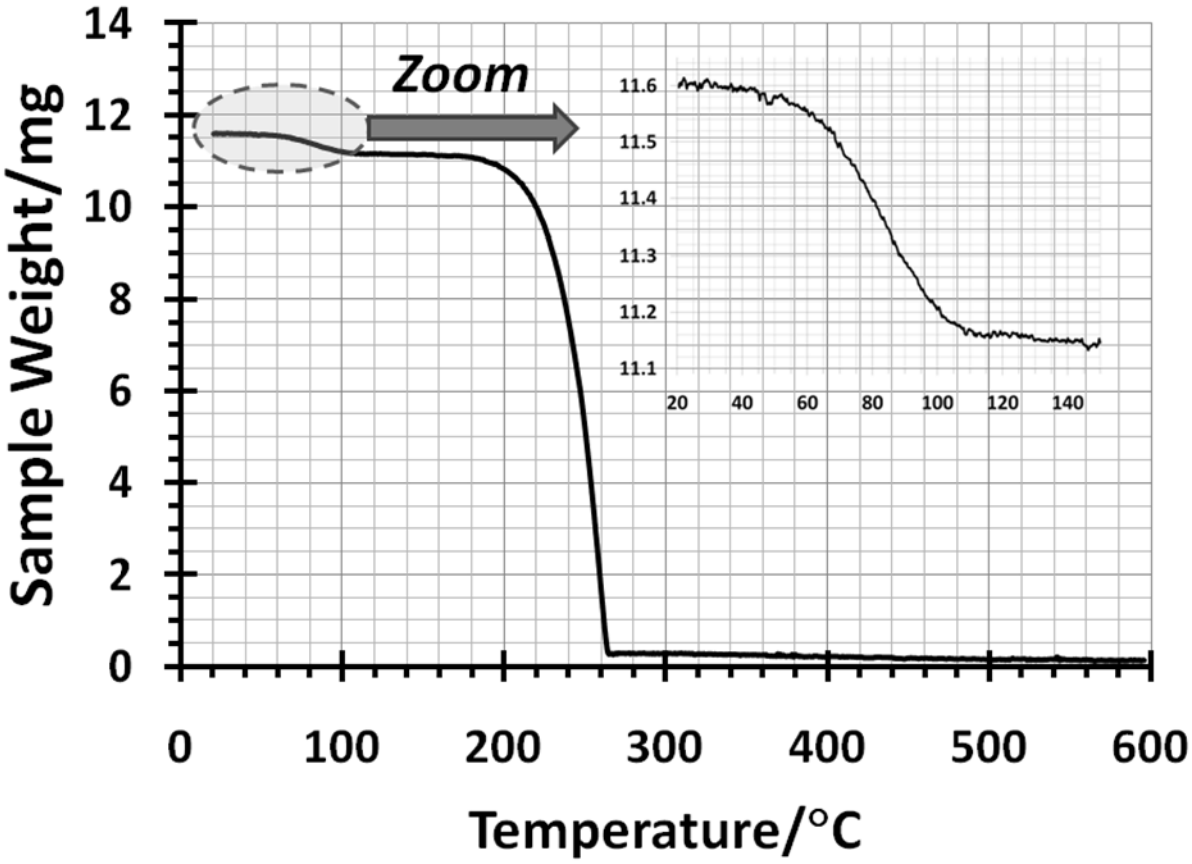

Figure S7. TGA for a toluene-exposed phosphorescent film of **1**.

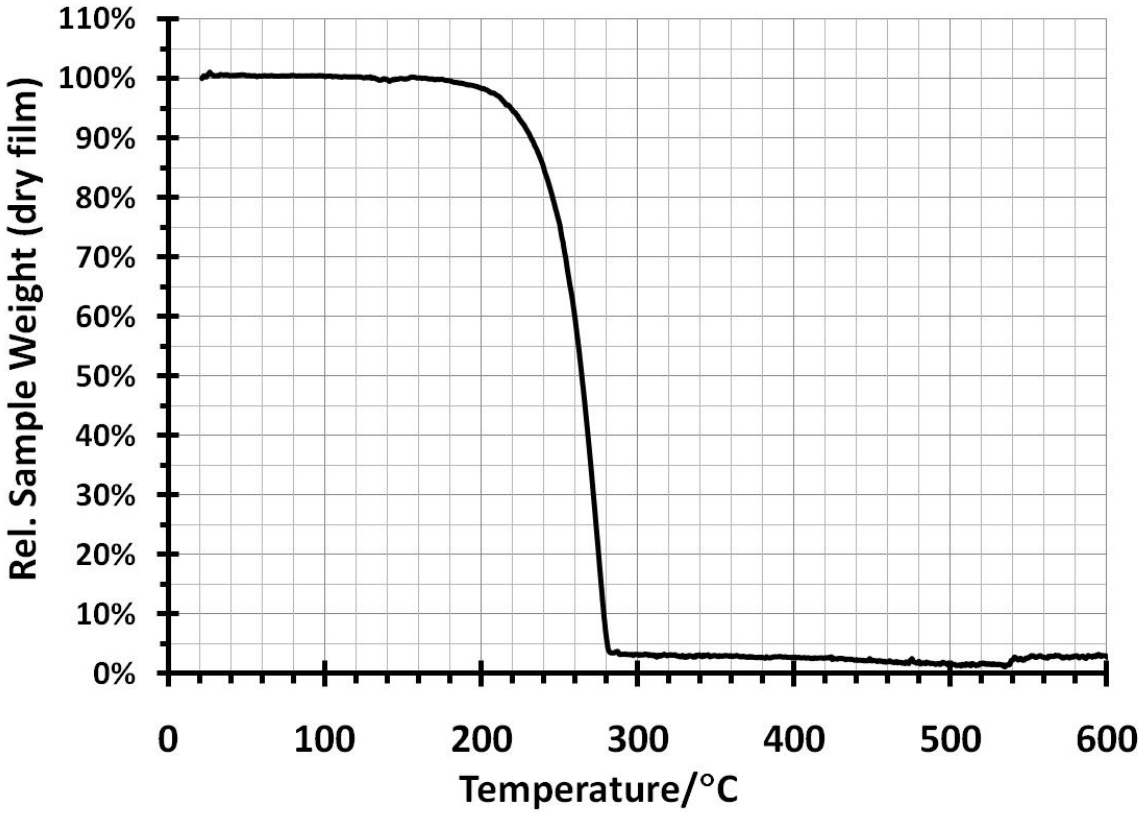

Figure S8. TGA for a dry nonluminescent film of **1**.

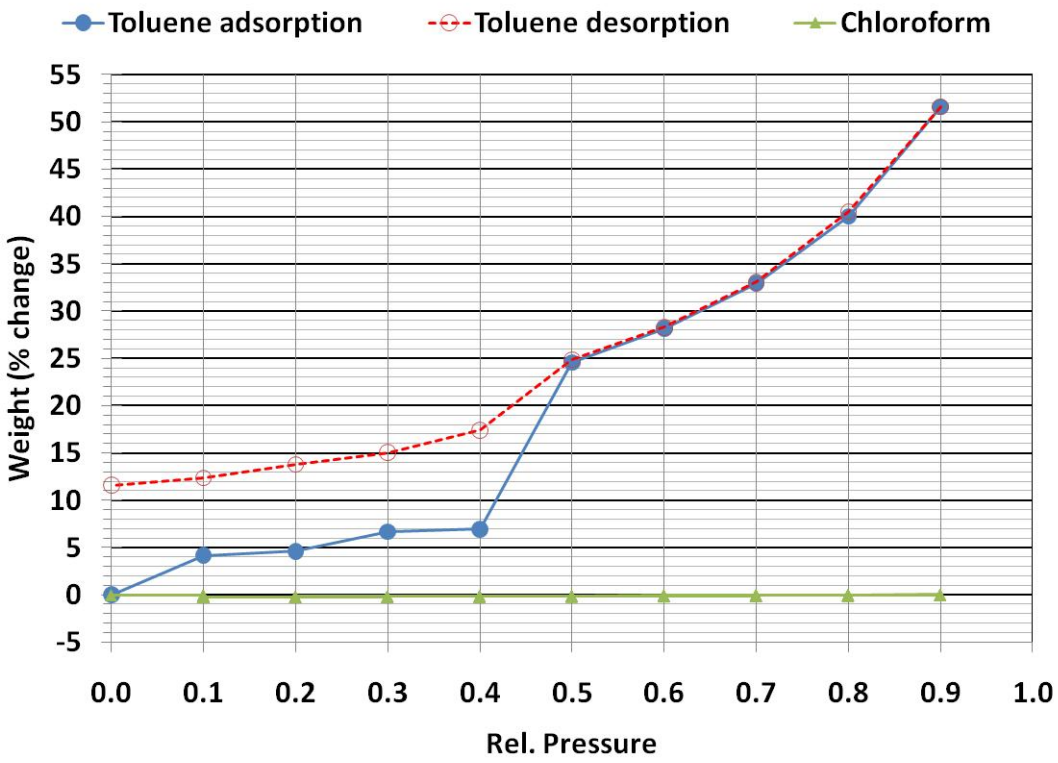

Figure S9. Adsorption/desorption isotherms for a powder sample of **1** upon exposure to toluene or chloroform up to P/P_o = 1.0. The solid sample dissolves at this high pressure and forms a transparent film after the experiment.

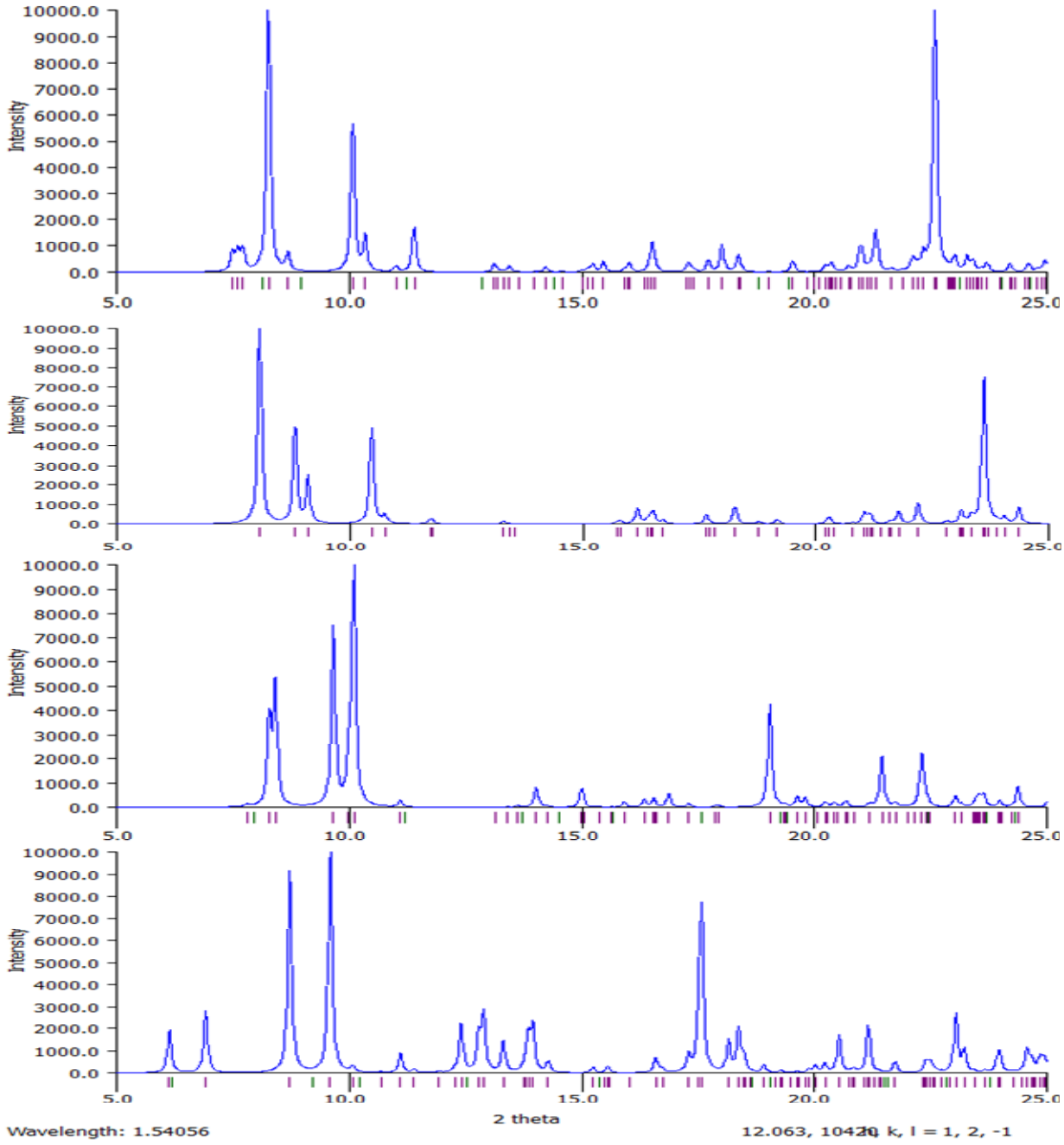

Figure S10. Simulated powder diffraction patterns for the single crystal data published earlier by Dias *et al.* (ref. 5) for two polymorphs of unsolvated samples (top two traces) and two polymorphs of benzene solvates (bottom two traces) of **1**. Note the prominence of the feature at 2θ = *ca.* 23 in the unsolvated samples and its diminishment in the solvated samples, consistent with the thin film data in the main manuscript (Fig. 2a).