

Electronic Supplementary Information

Reversible Mechanochromic Luminescence and Aggregation

Induced Emission for a Metal-Free β -Diketone

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Experimental

Materials

Solvents THF, and CH₂Cl₂, were dried by previously reported methods. Reactions were monitored using silica TLC plates. Compounds purchased from Sigma-Aldrich, and TCI were reagent grade and used without purification.

Methods

¹H NMR spectra (500 MHz) were recorded on a Varian Unity Inova spectrometer in deuterated DMSO. ¹³C NMR spectra (600 MHz) were recorded on a Varian Unity Inova spectrometer in deuterated DMSO. Spectra were referenced to the signals for residual protio-chloroform at 7.26 ppm, and protio-DMSO at 2.50 ppm and coupling constants were reported in Hz. Mass spectra were recorded using an Applied Biosystems 4800 spectrometer with a MALDI TOF/TOF analyzer. UV-vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. Steady-state fluorescence emission and excitation spectra were recorded on a Horiba Fluorolog-3 Model FL3-22 spectrofluorometer (double-grating excitation and double-grating emission monochromator). An excitation wavelength λ_{ex} of 369 nm was used for all emission spectra collected in solution and the solid state. Excitation spectra were monitored at 504 nm. Time-correlated single-photon counting (TCSPC) fluorescence lifetime measurements were performed with a NanoLED-370 ($\lambda_{\text{ex}} = 369$ nm) excitation source and a DataStation Hub as the SPC controller. Lifetime data were analyzed with DataStation v2.4 software from Horiba Jobin Yvon. Fluorescence quantum yields, Φ_{F} , in CH₂Cl₂ were calculated versus anthracene as the standard using the following values: Φ_{F} anthracene in ethanol = 0.27, n_{D} ethanol = 1.36, n_{D} CH₂Cl₂ = 1.424. Optically dilute

CH₂Cl₂ solutions of all samples were prepared in 1 cm path length quartz cuvettes with absorbances <0.1 (a.u.). Solid-state quantum yield were performed using a F-3029 Quanta-Φ Integrating Sphere from Horiba Scientific and analyzed using FluorEssence software. The sample morphologies of spin-cast films were characterized by Atomic Force Microscopy (AFM) (Digital Image, DI 3000) in tapping mode and the resulting images were processed using Gwyddion software version 2.31. Powder XRD patterns were obtained using a Panalytical X'Pert Pro MPD diffractometer operating at 40kV and 40 ma using Cu Kα radiation. Differential scanning calorimetry (DSC) was done on the pristine powders using a TA Instruments DSC 2920 Modulated DSC and were analyzed using the Universal Analysis software V 2.3 from TA Instruments. Thermograms were recorded using the standard mode and a temperature ramp rate of 5 °C/min from 0 to 200 °C. The second scan was reported. Thermograms were analyzed using TA Instruments Universal Analysis software V 2.3 .

Fabrication of aggregates for AIE measurements. A 10⁻³ M stock solution of dnmOMe in THF was prepared. Aliquots of 100 μL of the stock solution were added to 10 mL volumetric flasks and diluted to volume with THF and H₂O in the proper ratios. Solutions were placed in a sonicator for 10 min before measuring absorption and emission spectra

Preparation of solutions for pH sensitivity measurements. A 2.25 mM solution of dnmOMe in CH₃CN was prepared and 1 mL portions of the stock solutions were added to three separate 10 mL volumetric flasks, which contained (1) no TEA or acetic acid, (2) TEA (0.457 g, 0.45 mM), (3) TEA (0.457 g, 0.45 mM) and acetic acid (0.409 g, 0.68 mM), respectively. Each solution was diluted to volume with CH₃CN and placed in the sonicator for 10 min prior to taking measurements.

Preparation of dnmOMe thin films. Thin films used for AFM, XRD, and ML characterization were prepared on 22 mm diameter glass coverslips purchased from Fisher Scientific. Solid-state quantum yield measurements were performed on films cast on glass coverslips with 12 mm diameter. With the exception of spin-cast films subjected to XRD, the films were fabricated by preparing 10^{-3} M solutions and applying ~ 10 drops to the coverslips rotating at 3,000 rpm. The films were dried *in vacuo* for 15 min before measurements or thermal annealing. Thin films subjected to XRD analysis were made from a saturated dnmOMe stock solution on 25 mm diameter glass slides and were prepared by applying ~ 10 drops of the stock solution to the slides spinning at 1000 rpm.

Synthesis of dnmOMe. The ligand dnmOMe was prepared by Claisen condensation of 2-acetyl-6-methoxynaphthalene (0.543 g, 2.71 mmol) and methyl-2-naphthoate (0.626 g, 3.40 mmol) in the presence of NaH. The reactants were dissolved in THF (50 mL) prior to the dropwise addition of a NaH/THF (10 mL) suspension under N_2 . The reaction was heated to 60 °C and stirred for 20 h before quenching with 1 mL of a saturated $NaHCO_3$ solution (aq). Aqueous phases were extracted with CH_2Cl_2 (3 x 50 mL) and combined organic layers were washed with a dilute HCl solution (3 x 50 mL) and brine (10 mL). Organic layers were dried over Na_2SO_4 prior to the removal of solvent. The ligand dnmOMe was recrystallized twice from 1:1 hexanes/acetone mixture and recovered was recovered as a white powder (0.228 g, 24%). 1H NMR (500 MHz, DMSO- d_6) δ 17.36 (s, 1H, -OH) 8.87 (s, 1H, 1''-ArH) 8.82 (s, 1H, 1'-ArH) 8.25 (d, J = 9, 1H, 4''-ArH) 8.22 (d, J = 9, 1H, 4'-ArH) 8.15 (d, J = 9, 1H, 3''-ArH) 8.10-8.01 (m, 3H, 8'',5'',8'-ArH) 7.98 (d, J = 9, 1H, 3'-ArH) 7.68-7.63 (m, 3H, 7'',6''-ArH, COCHCO) 7.45 (s, 1H, 5'-ArH) 7.28 (d, J = 9, 1H, 7'-ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 186.01, 184.80, 159.56, 135.26, 132.87,

132.78, 130.98, 130.71, 129.34, 128.44, 128.27, 128.21, 128.15, 128.06, 127.76, 127.19, 126.76, 123.99, 123.27, 119.76 105.75, 93.40, 55.42; HRMS (ESI, TOF): m/z calculated for C₂₄H₁₉O₃ 355.13; found 355.13 [M+H]⁺.

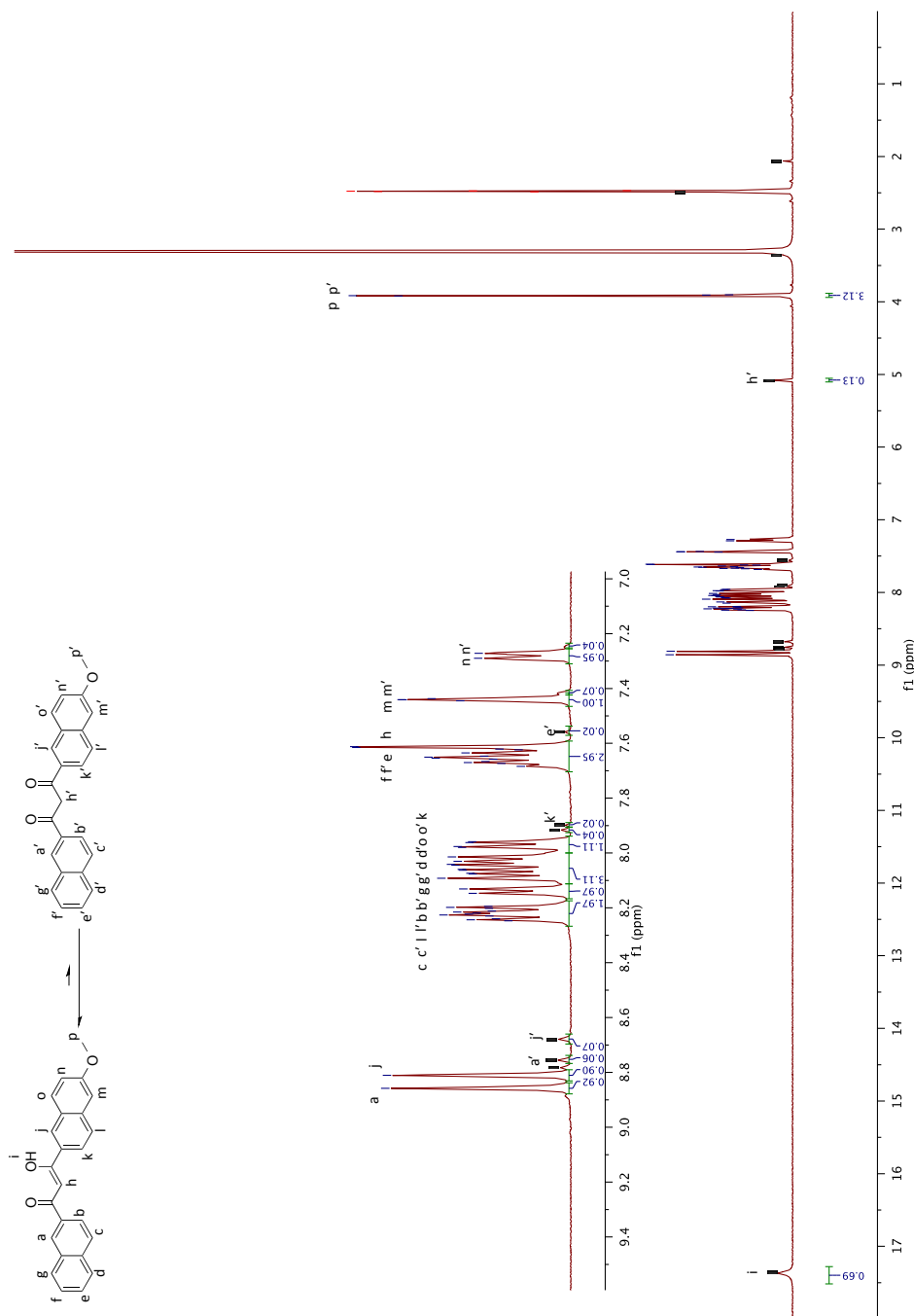


Fig S1. ¹H NMR spectrum of dnmOMe in deuterated DMSO.

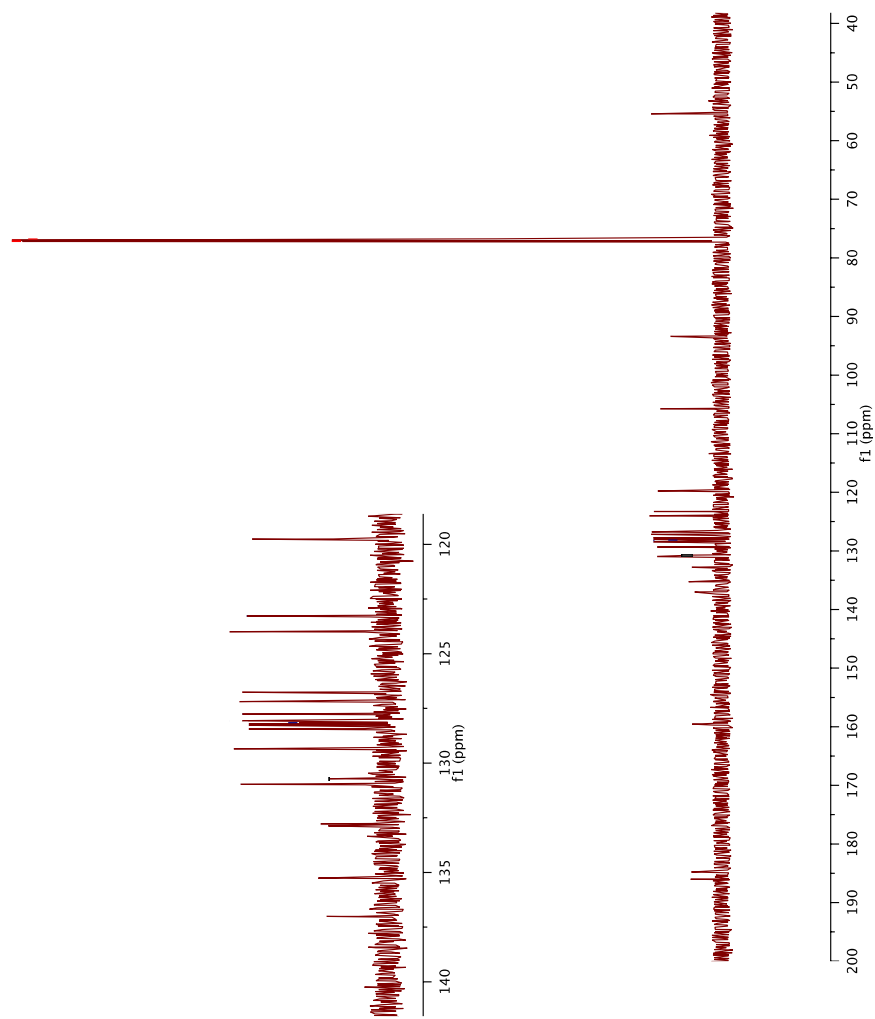


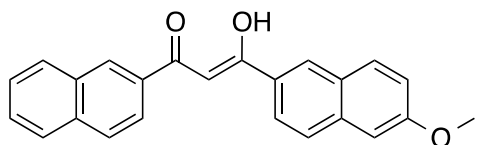
Fig S2. ^{13}C NMR spectrum of dnmOMe in CDCl_3 .

Full Computational Details

The compound dnmOMe was modeled using the Gaussian 09 suite of programs¹ utilizing density functional theory (DFT). We chose B3LYP/6-31G(d) for ground state geometry optimization with a Tomasi polarized continuum for dichloromethane solvent.² The vibrational frequencies for the optimized geometries were calculated in an additional calculation also utilizing B3LYP/6-31G(d). All vibrational frequencies were positive, assuring that the geometries were at least a local minimum. Single point energy calculations were used to generate the molecular orbital diagrams utilizing B3LYP/6-31G(d). Time-dependent density functional theory (TD-DFT), TD-B3LYP/6-31+G(d) was used for estimates of the absorption spectra at the respective optimized geometries.^{3,4} The first three excited states were computed for dnmOMe. Molecular orbitals were depicted by GaussView 5 software.⁵

Gaussian 09 Specifications for dnmOMe in CH₂Cl₂ Solvent. B3LYP/6-31G(d) optimized structure for future TD-DFT calculation in dichloromethane. Coordinates are given in Cartesian, in Angstroms.

E (HF) = -1151.09786328. μ (Debye) = 4.1691

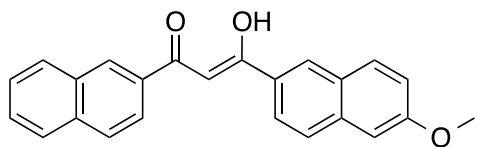


O, -2.125439, 2.230985, -0.305982
C, -2.078267, 0.96992, -0.222565
C, -0.822312, 0.273779, -0.17245
H, -0.806001, -0.79652, -0.038154
O, 0.388785, 2.292695, -0.343117
C, 0.375192, 0.965014, -0.235274
C, 1.705332, 0.337839, -0.181029
C, 2.831691, 1.136928, -0.045294

C, 1.875408, -1.078695, -0.263699
C, 4.130421, 0.579899, 0.022269
H, 2.717742, 2.21407, 0.016984
C, 3.12234, -1.645668, -0.204027
H, 1.011621, -1.721128, -0.394871
C, 4.292272, -0.843686, -0.056243
C, 5.290796, 1.384475, 0.166672
H, 3.232936, -2.72449, -0.275264
C, 5.587337, -1.398444, 0.009933
C, 6.548503, 0.826772, 0.229892
H, 5.177533, 2.463774, 0.227388
C, 6.701895, -0.584399, 0.150567
H, 5.725583, -2.474133, -0.048806
H, 7.414073, 1.469085, 0.339711
C, -3.365226, 0.213919, -0.156686
C, -3.443425, -1.197926, -0.337421
C, -4.529999, 0.924715, 0.084255
C, -4.651904, -1.849134, -0.269154
H, -2.548627, -1.770284, -0.556228
C, -5.788717, 0.282051, 0.169203
H, -4.468905, 2.000649, 0.214549
C, -5.856305, -1.139099, -0.010272
H, -4.699815, -2.924919, -0.418142
C, -6.988291, 1.003036, 0.426083
C, -7.119384, -1.783029, 0.072911
C, -8.197612, 0.34936, 0.50099
H, -6.93224, 2.080227, 0.561604
C, -8.263043, -1.056008, 0.322788
H, -7.169528, -2.860388, -0.063985
H, -9.10844, 0.907974, 0.697052
H, -9.224034, -1.559109, 0.384582
O, 7.906078, -1.215808, 0.204614
C, 9.091175, -0.434278, 0.348152
H, 9.914491, -1.149553, 0.366187
H, 9.224349, 0.25108, -0.497098
H, 9.084744, 0.135346, 1.284818
H, -0.588134, 2.571294, -0.342049

Characterization of Spectrum Computed in Solvent Dichloromethane (PCM-Tomasi as implemented in Gaussian).

Note: Max amplitude is 0.70714 for a pure one-electron excitation. The highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) transitions are in bold.



Excited State 1: Singlet-A 3.0005 eV 413.21 nm f=0.9707 <S2>=0.000**
93 -> 94 0.69887

Excited State 2: Singlet-A 3.2780 eV 378.23 nm f=0.0601 <S**2>=0.000
92 -> 94 0.69187

Excited State 3: Singlet-A 3.5607 eV 348.20 nm f=0.3753 <S**2>=0.000
91 -> 94 0.67509
93 -> 96 0.12882

Gaussview traces of computed TD-B3LYP/6-31+G(d) absorption spectra for dnmOMe in CH₂Cl₂ represented by Tomasi's Polarizable Continuum Model.

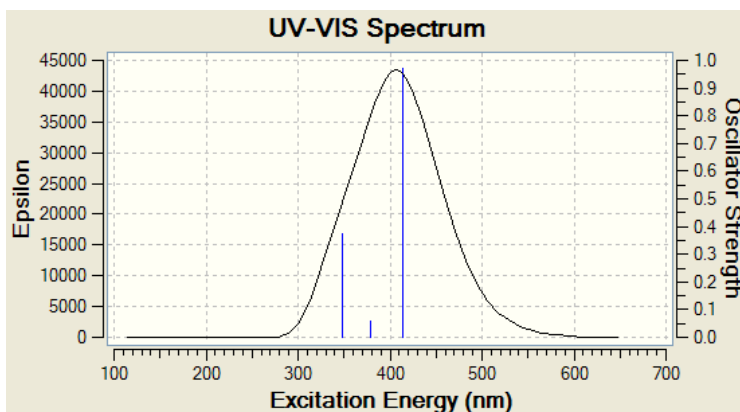


Fig S3. Calculated absorption spectrum of dnmOMe in CH₂Cl₂.

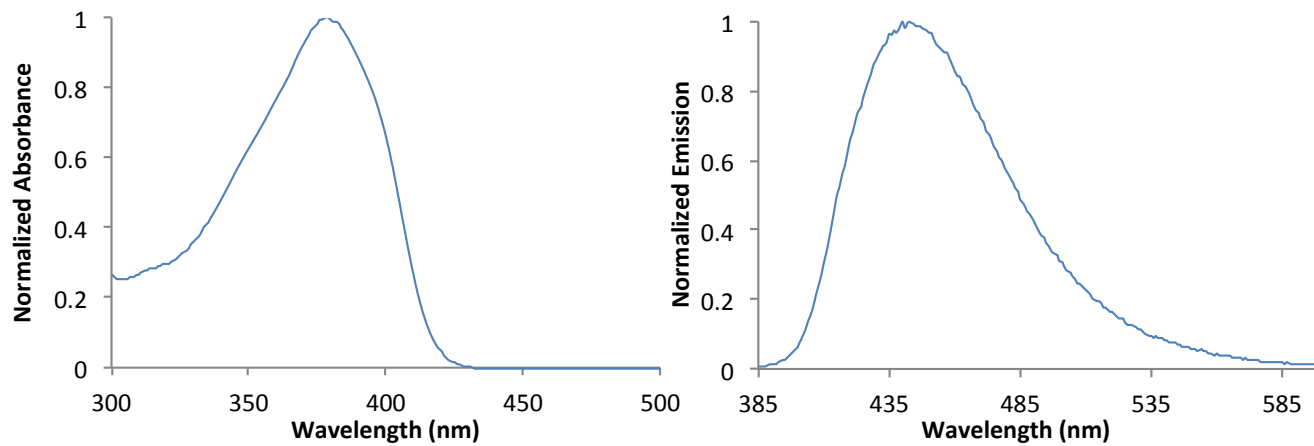


Fig S4. Absorption (left) and emission (right) of dnmOMe in CH_2Cl_2 ($\lambda_{\text{ex}} = 369 \text{ nm}$).

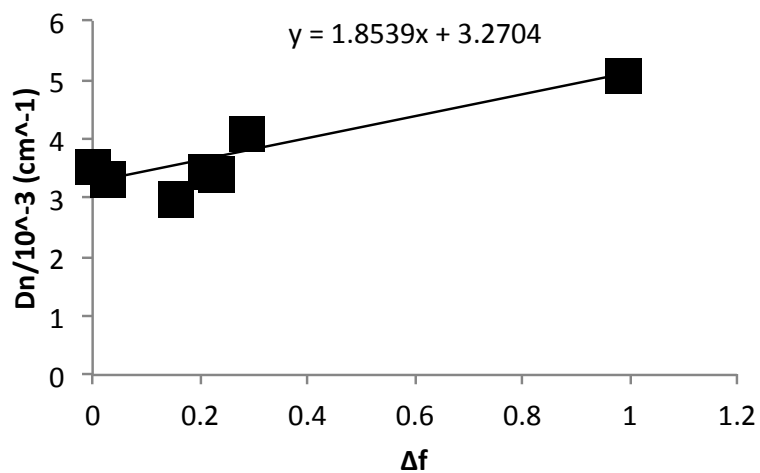


Fig. S5. Lippert-Mataga plot of dnmOMe solvatochromism.

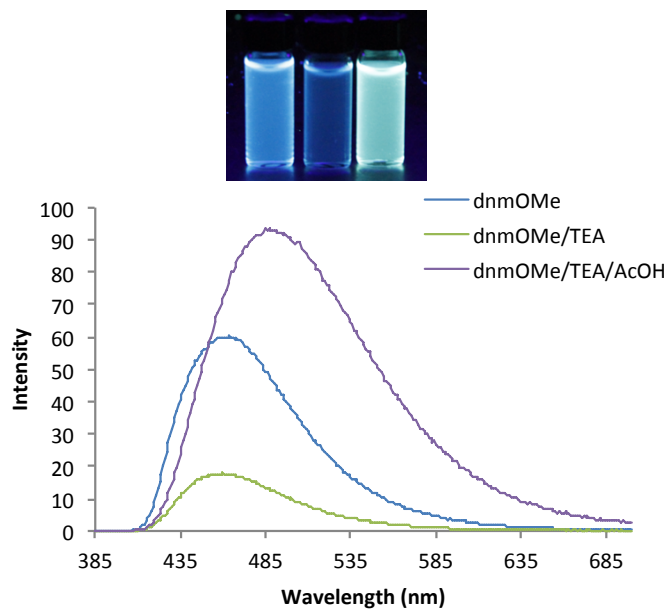


Fig. S6. Solutions of dnmOMe in CH₃CN, CH₃CN/TEA, and CH₃CN/TEA/acetic acid, respectively (top). Emission spectra of solutions (bottom) ($\lambda_{\text{ex}} = 369$ nm).

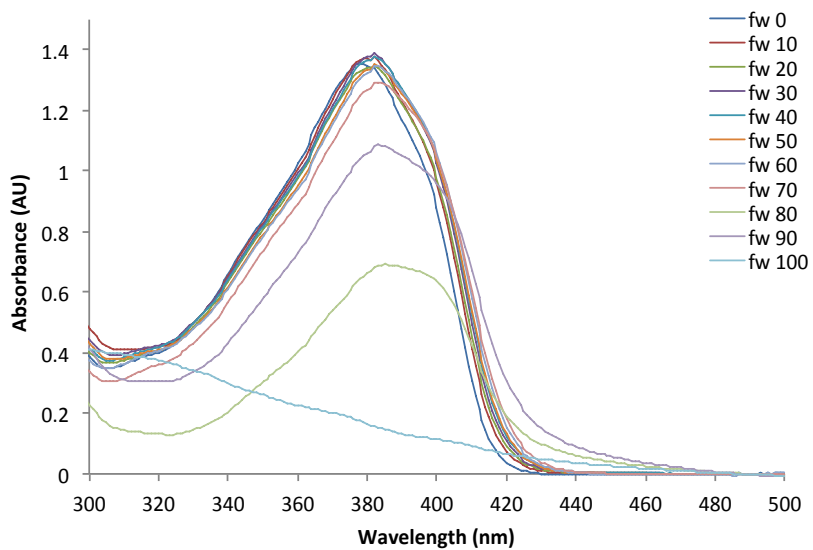


Fig. S7. Absorption spectra of dnmOMe in THF/H₂O solutions.

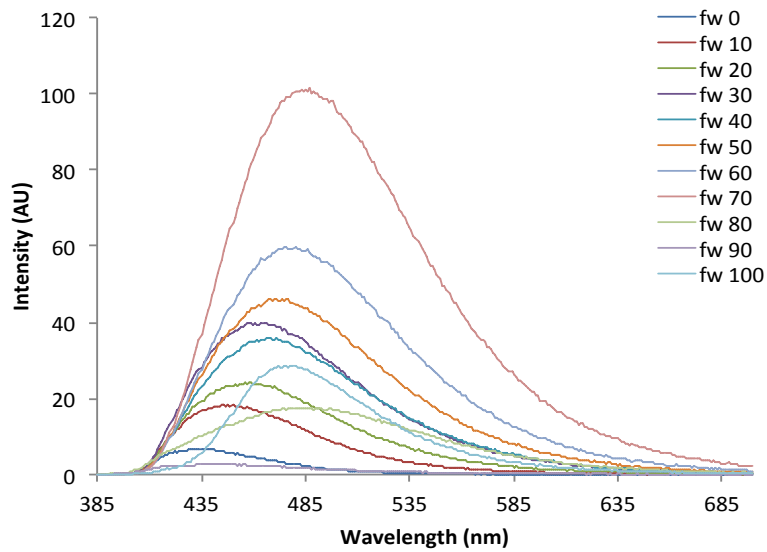


Fig. S8. Emission spectra of dnmOMe in THF/H₂O solutions ($\lambda_{\text{ex}} = 369$ nm).

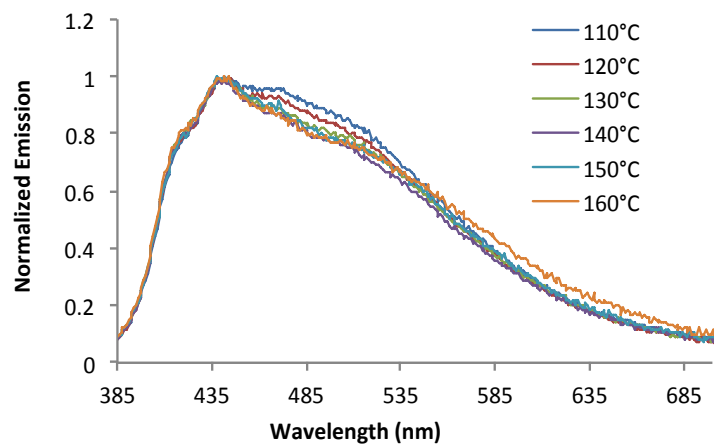


Fig. S9. Emission spectra of dnmOMe annealed at different temperatures ($\lambda_{\text{ex}} = 369$ nm).

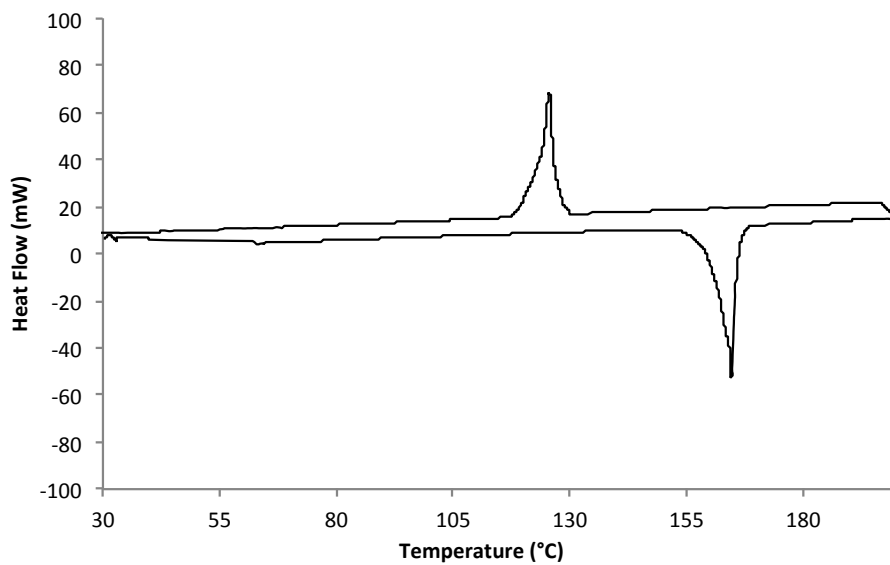


Fig. S10. DSC thermogram of dnmOMe.

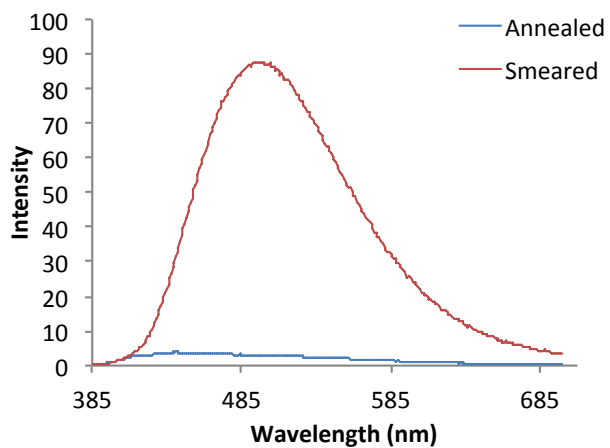


Fig. S11. Total emission spectra of dnmOMe thin films in smeared and annealed states ($\lambda_{\text{ex}} = 369 \text{ nm}$).

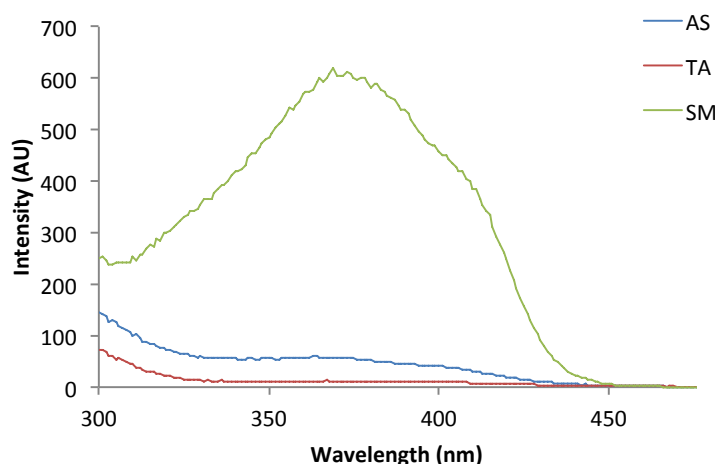


Fig. S12. Excitation spectra of dnmOMe in AS, TA and SM states monitored at 504 nm.

References

1. M. J. Frisch, G. W Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y Honda, O Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, R. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, J. J. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, A. Farkas, J. B. Foresman, J. Ortiz, J. Cioslowski, D. J. Fox, Wallingford CT, 2009.
2. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 2005, **105**, 2999.
3. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 1372.
4. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.
5. R. Dennington, T. Keith, 5th Ed.; Semichem Inc.: Shawnee Mission, KS, 2009.