Supporting Information

Mechanochromic Luminescence and Aggregation Induced Emission of Dinaphthoylmethane β-Diketones and their Boronated Counterparts

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DnmBr. Tan powder: 0.607 g, 46%. ^{1}H NMR (300 MHz, DMSO-d6) δ 17.26 (s, 1H, ArCOH), 8.90-8.89 (m, 2H, 1″,1′-ArH), 8.35 (s, 1H, 5′-ArH), 8.31 (d, J = 9, 1H, 4″-ArH), 8.25 (d, J = 9, 1H, 4′-ArH), 8.16-8.08 (m, 4H, 8′,8″,7′-ArH, COCHCO), 8.04 (d, J = 9, 5″-ArH), 7.77 (d, J = 9, 1H, 3″-ArH) 7.71-7.62 (m, 3H, 7″,6″,3′-ArH). HRMS (ESI, TOF): m/z calculated for $C_{23}H_{16}O_2Br$ 403.0327; found 403.0334 [M+H].

DnmBrOMe. Brown powder: 0.455 g, 37%. ^{1}H NMR (300 MHz, DMSO-d6) δ 17.50 (s, 1H, ArCOH), 8.87 (s, 1H, 1″-Ar*H*), 8.81 (s, 1H, 1′-ArH), 8.33 (s, 1H, *5*′-ArH), 8.29 (d, J = 9, 1H, 4″-ArH), 8.20 (s, J = 9, 1H, 4′-ArH), 8.12-8.03 (m, 3H, 8′, 8″, 5′-ArH), 7.98 (d, J = 9, 1H, 3′-ArH), 7.77 (d, J = 9, 1H, 7′-ArH), 7.62 (s, 1H, COCHCO), 7.44 (s, 1H, 5′-ArH), 7.29 (d, 1H, 7″-ArH), 3.92 (s, 3H, OCH_3). HRMS (ESI, TOF): m/z calculated for $C_{24}H_{18}O_3Br$ 433.0445; found 433.0439 [M+H].

BF_2dnmOMe. Yellow powder: 0.145 g, 42%. ^{1}H NMR (300 MHz, DMSO-d6) δ 9.13 (s, 1H, 1″-ArH), 9.10 (s, 1H, 1′-ArH), 8.40-8.38 (m, 2H, 4″,4′-ArH), 8.24 (d, J = 9, 1H, 3″-ArH), 8.20-8.15 (m, 4H, 7″,7′,3′-ArH, COCHCO), 8.10-8.04 (m, 2H, 8″,8′-ArH), 7.79-7.70 (m, 1H, 6′-ArH), 7.52 (s, 1H, 5″-ArH), 7.34 (d, J = 9, 1H, 5′-ArH), 3.95 (s, 3H, OCH_3). HRMS (ESI, TOF): m/z calculated for $C_{24}H_{17}BO_3F$ 383.1255; found 383.1255 [M-F].

BF_2dnmBr. After recrystallization (2×) from 1:1 acetone/THF, a yellow solid was obtained: 0.078 g, 17%. ^{1}H NMR (500 MHz, DMSO-d6) δ 9.18 (s, 2H, 1″,1′-ArH), 8.47 (d, J = 9, 1H, 4″-ArH), 8.42-8.39 (m, 2H, COCHCO, 4′-ArH), 8.23-8.17 (m, 5H, 8″,8′,5″,3″,3′-ArH), 8.11 (d, J = 9, 1H, 5′-ArH), 7.86 (d, J = 9, 1H, 7′-ArH), 7.79 (t, J = 5, 1H, 7″-ArH), 7.72 (t, J = 5, 1H, 6″-ArH). HRMS (ESI, TOF): m/z calculated for $C_{23}H_{14}BO_2FBr$ 431.0254; found 431.0260 [M-F].

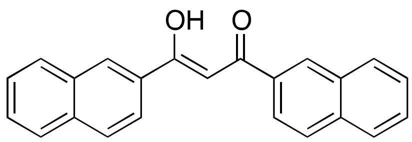
BF_2dnmBrOMe. After recrystallization (3×) from toluene, an orange powder was obtained: 0.038 g, 11% yield. ^{1}H NMR (500 MHz, DMSO-d6) δ 9.13 (s, 1H, 1″-ArH), 9.10 (s, 1H, 1′-ArH), 8.46-8.36 (m, 3H, COCHCO, 4″,4′-ArH), 8.21-8.16 (m, 2H, 8″,5″-ArH), 8.07 (d, 1H, J = 9, 8′-ArH), 7.85 (d, J = 9, 1H, 3″-ArH) 7.52 (s, 1H, 5′-ArH), 7.36 (d, J = 9, 1H, 3″-ArH), 7.24 (d, J = 9, 1H, 7″-ArH), 7.17 (d, J = 9, 1H, 7′-ArH), 3.96 (s, 3H, OCH_3); HRMS (ESI, TOF): m/z calculated for $C_{24}H_{16}O_3BrFB$ 461.0366; found 461.0360 [M-F].

Full Computational Details

All compounds were modeled using the Gaussian 09 suite of programs[1] utilizing density functional theory (DFT). We chose B3LYP/6-31G(d) for ground state geometry optimization of the ligands 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). The same calculations were used for the boronated complexes except that the more flexible B3LYP/6-31+G(d) was used. Calculations performed on the ligands using B3LYP/6-31+G(d) tended to crash, possibly due to the greater degree of rotational freedom available to the ligands compared to the complexes. 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) for both the ligands and the boronated complexes. Molecular orbitals were depicted by GaussView 5 software.[3]

Gaussian 09 Specifications for all ligands and compounds in CH_2Cl_2 Solvent. B3LYP/6-31G(d) optimized structure for ligands and B3LYP/6-31+G(d) for boron compounds.

Coordinates are given in Cartesian, in Angstroms. Molecular Orbitals were depicted by GaussView 5 software.[6]



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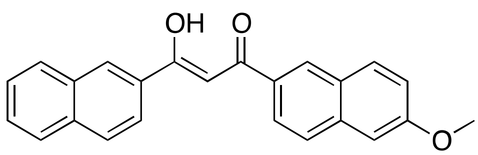

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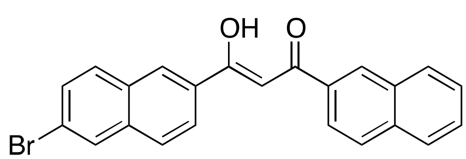

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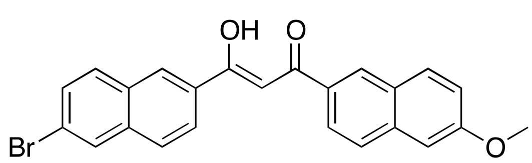

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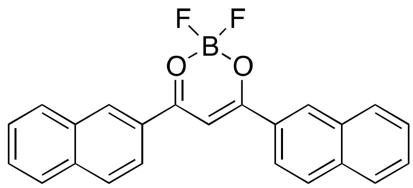

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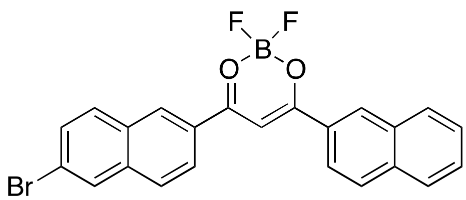

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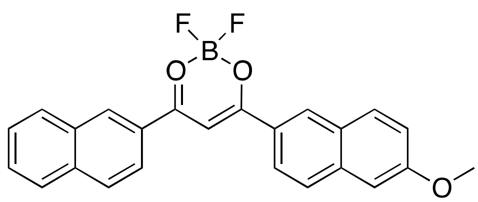

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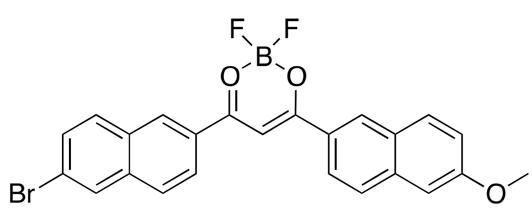

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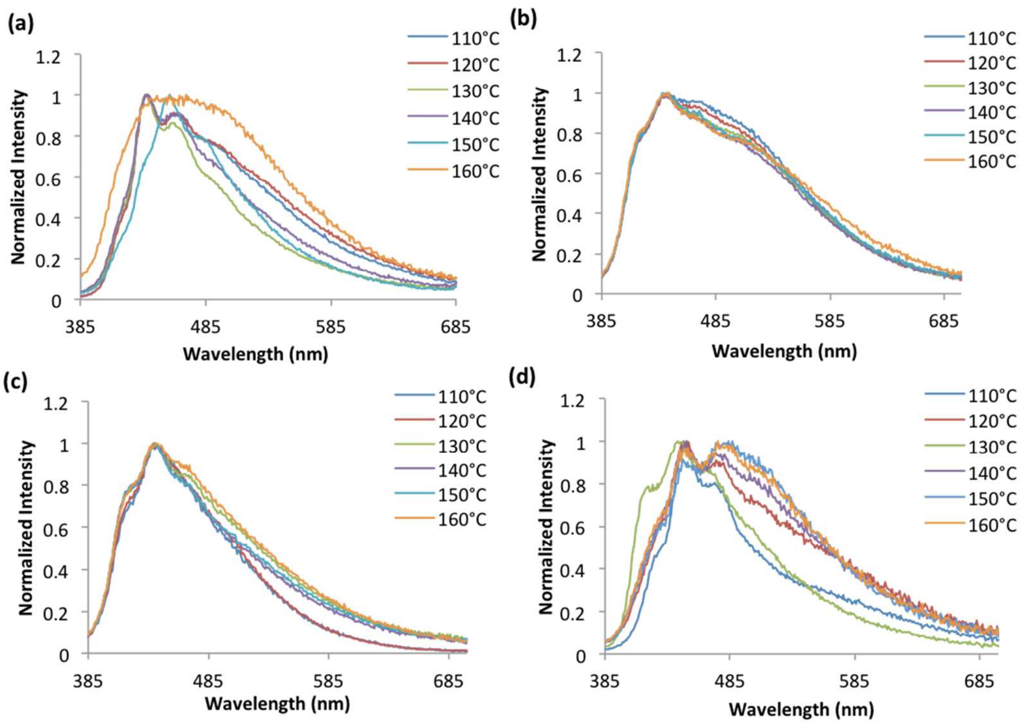

Fig. S1.Emission spectra of dnm (a), dnmOMe (b), dnmBr (c), dnmBrOMe (d) thin films annealed at different temperatures (°C) (λ_{ex} = 369 nm).

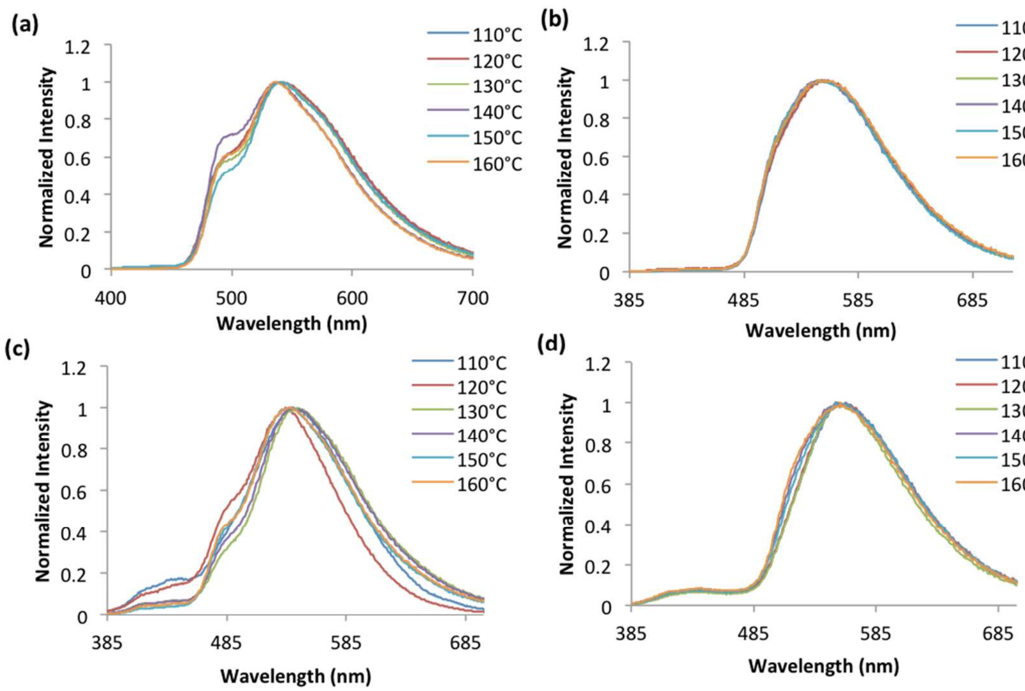

Fig. S2. Emission spectra of BF_2dnm (a), BF_2dnmOMe (b), BF_2dnmBr (c), BF_2dnmBrOMe (d) thin films annealed at different temperatures (λ_{ex} = 369 nm).

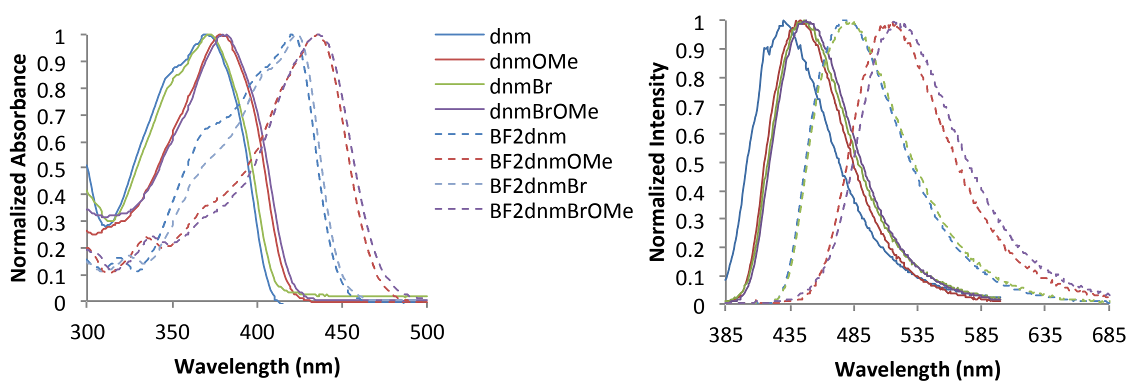

Fig. S3. Absorption (left) and emission (right) spectra of ligands and boron compounds (λ_{ex} = 369 nm).

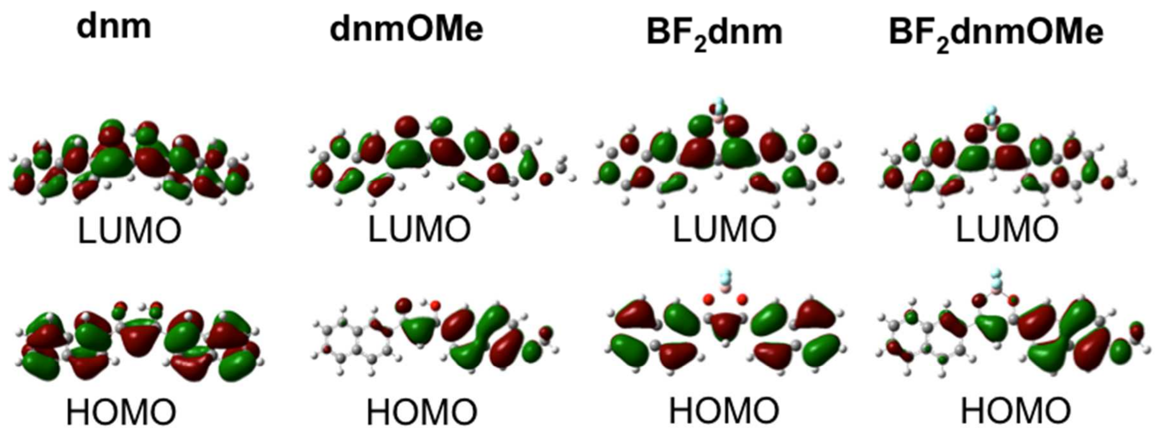

Fig. S4. Frontier molecular orbitals of dnm, dnmOMe and boron derivatives BF_2dnm and BF_2dnmOMe.

Table S1. Melting Points for Ligands and Boron Complexes

Compound	**Melting Temperature (°C)**
dnm	162-164
dnmOMe	158-160
dnmBr	201-202
dnmBrOMe	250-255
BF_2dnm	326-329
BF_2dnmOMe	280-284
BF_2dnmBr	299-301
BF_2dnmBrOMe	343-345

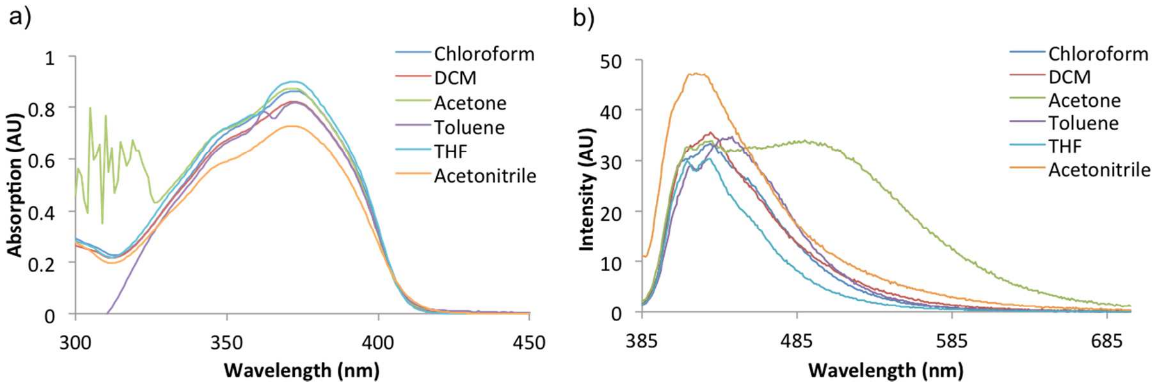

Fig. S5. Absorption (a), and emission (b) spectra of dnmBr in varying solvents. Solvents, from left to right: chloroform, $CHCl_2$, acetone, toluene, THF, acetonitrile (λ_{ex} = 369 nm).

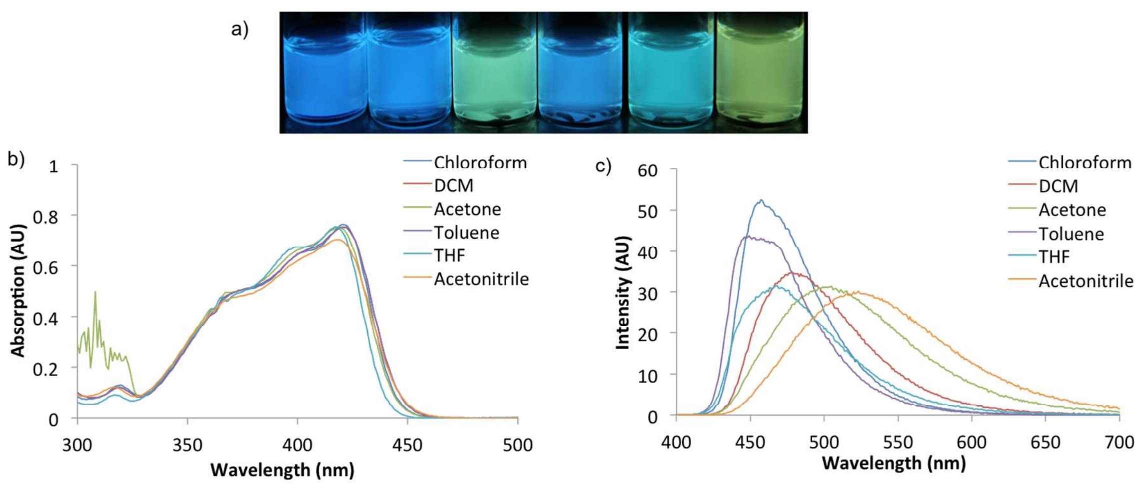

Fig. S6. Photo under UV irradiation (a), absorption (b), and emission (c) spectra of BF_2dnm in varying solvents. Solvents, from left to right: chloroform, $CHCl_2$, acetone, toluene, THF, acetonitrile (λ_{ex} = 369 nm).

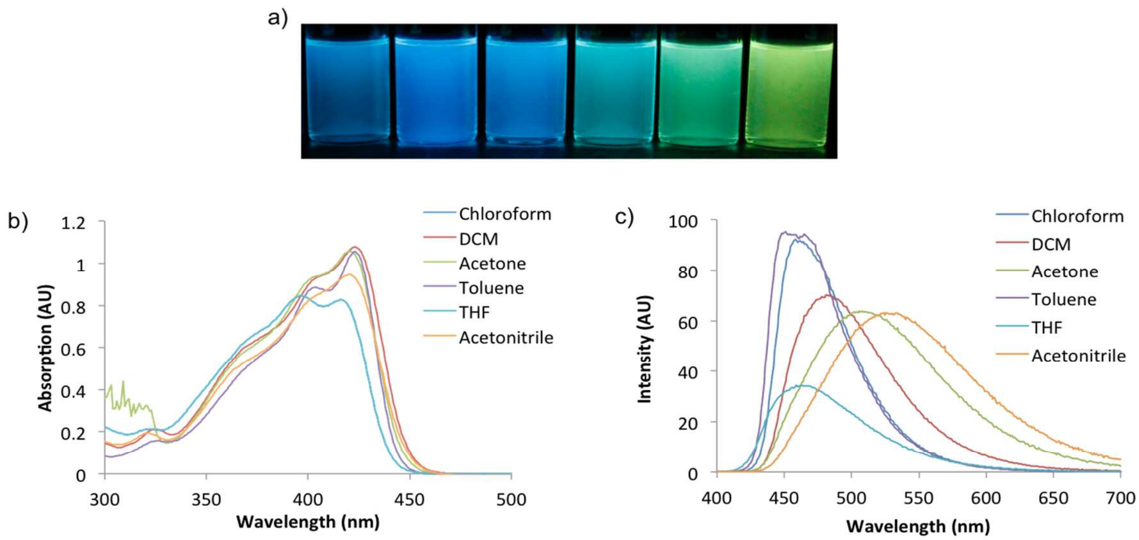

Fig. S7. Photo under UV irradiation (a), absorption (b), and emission (c) spectra of BF_2dnmBr in varying solvents. Solvents, from left to right: chloroform, $CHCl_2$, acetone, toluene, THF, acetonitrile (λ_{ex} = 369 nm).

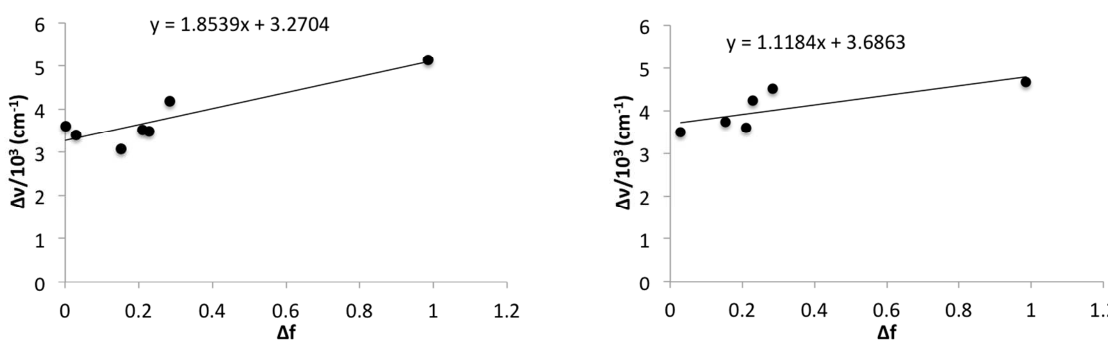

Fig S8. Lippert-Mataga plots of dnmOMe and dnmBrOMe solvatochromism.

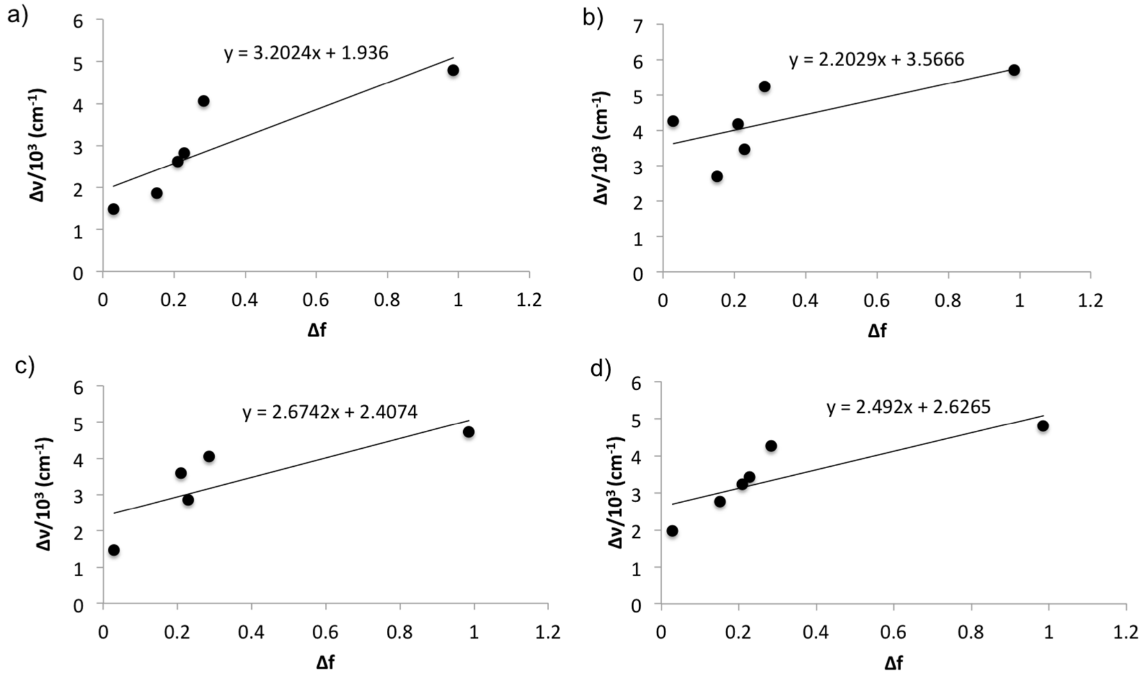

Fig. S9. Lippert-Mataga plots of BF_2dnm (a), BF_2dnmOMe (b), BF_2dnmBr (c), and BF_2dnmBrOMe (d) solvatochromism.

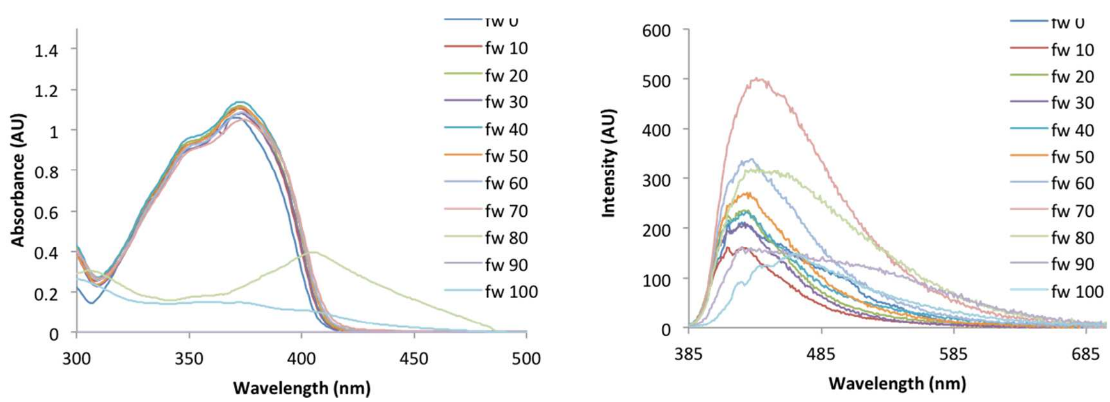

Fig S10. Absorption (a) and emission (b) spectra of dnm in different THF/H_2O mixtures (λ_{ex} = 369 nm).

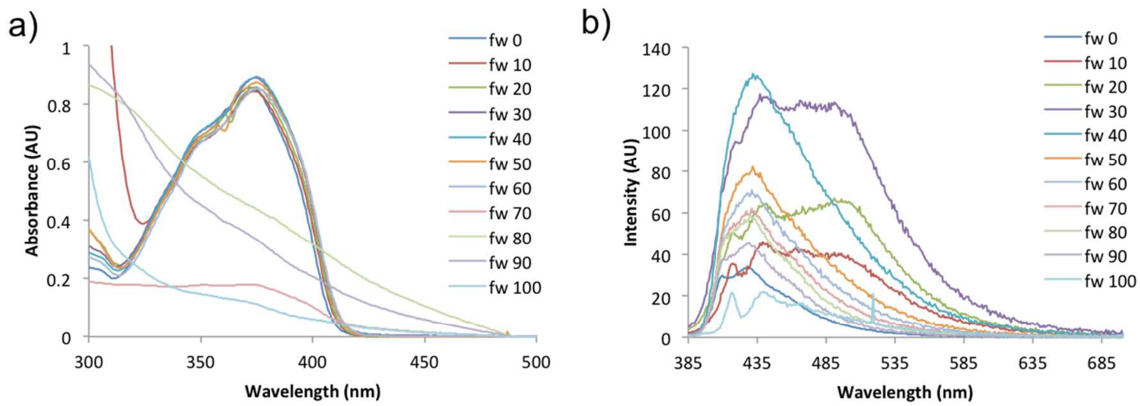

Fig S11. Absorption (a) and emission (b) spectra of dnmBr in different THF/H_2O mixtures (λ_{ex} = 369 nm).

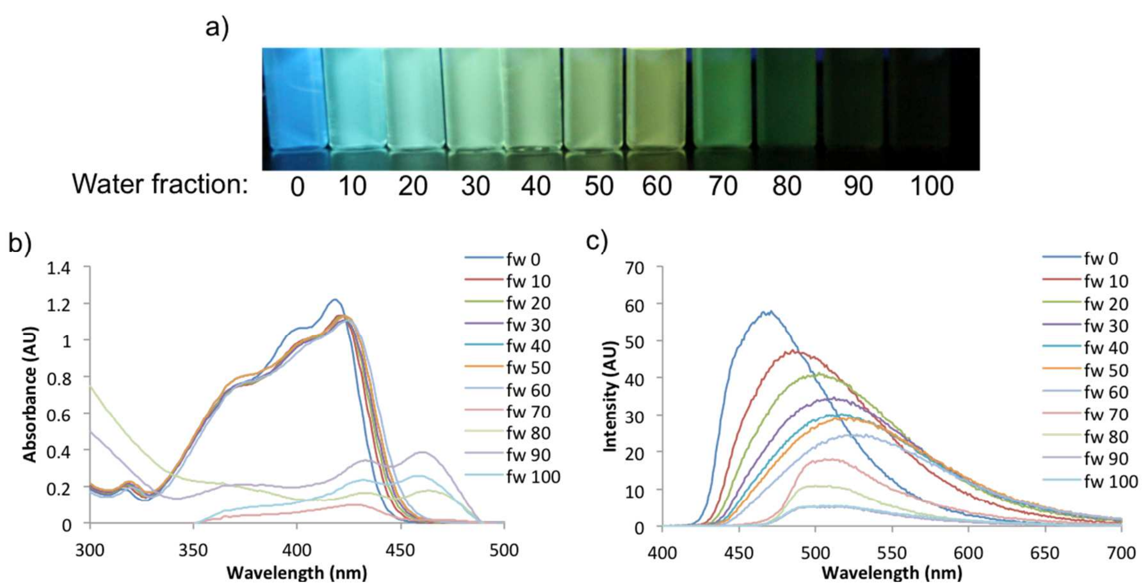

Fig. S12. Image under UV irradiation (a), and corresponding absorption (b) and emission (c) spectra of BF_2dnm in different THF/H_2O mixtures (λ_{ex} = 369 nm).

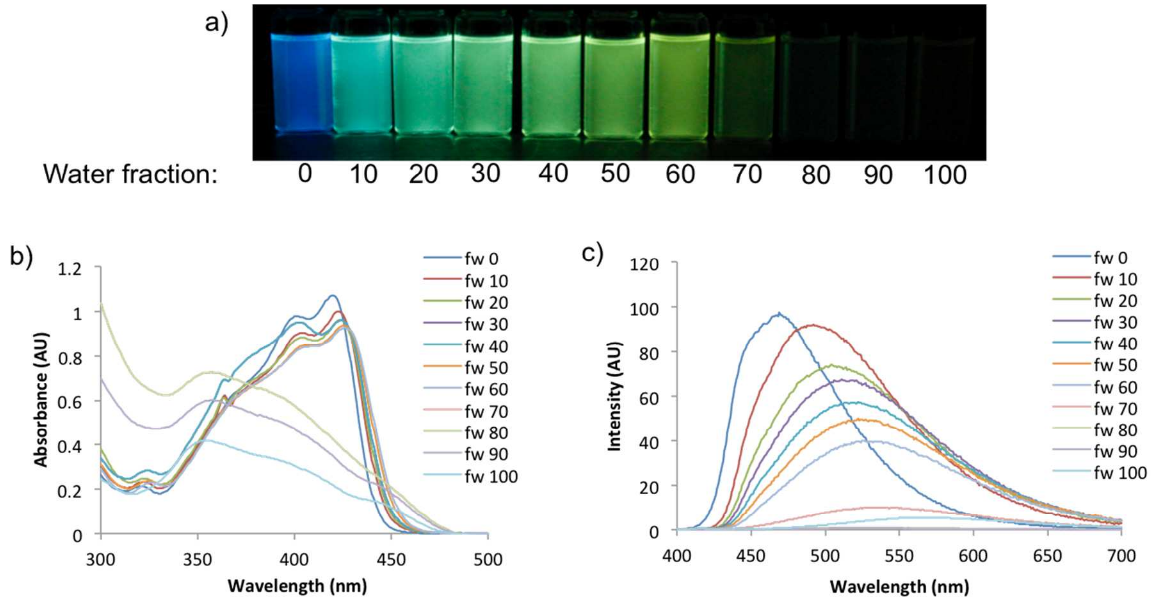

Fig. S13. Image under UV irradiation (a), and corresponding absorption (b) and emission (c) spectra of BF_2dnmBr in different THF/H_2O mixtures (λ_{ex} = 369 nm).

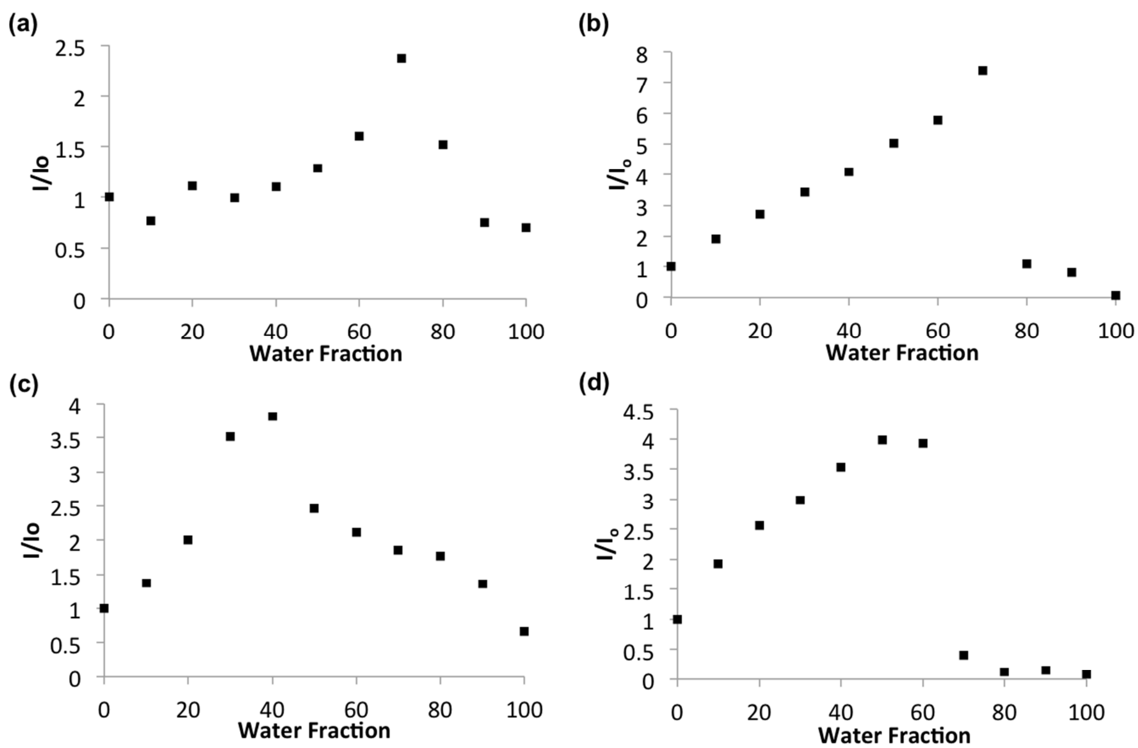

Fig. S14. Plots of I/I_o versus water fraction for dnm (a), dnmOMe (b), dnmBr (c), and dnmBrOMe (d).

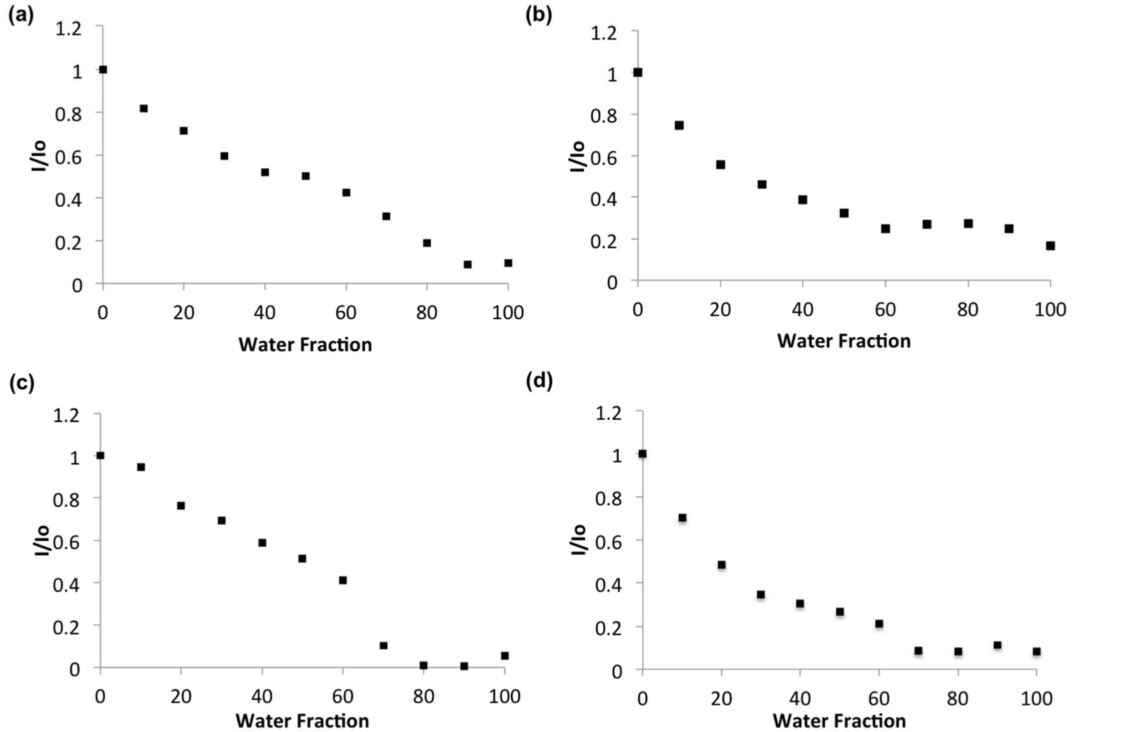

Fig. S15. Plots of I/I_o versus water fraction for BF_2dnm (a), BF_2dnmOMe (b), BF_2dnmBr (c), and BF_2dnmBrOMe (d).

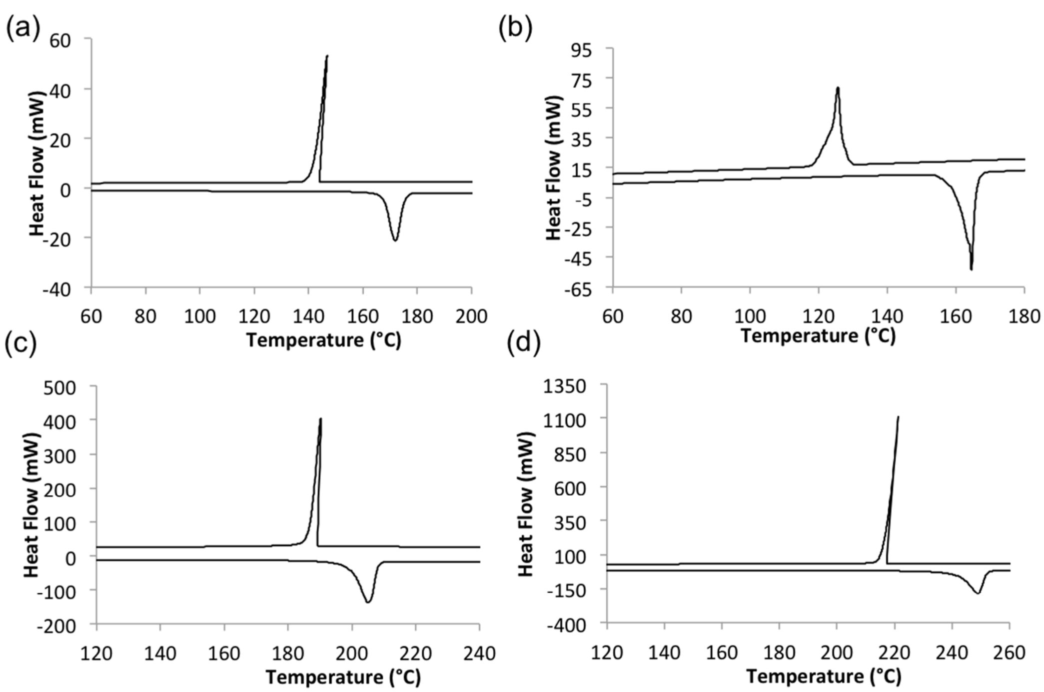

Fig. S16. DSC thermograms of dnm (a), dnmOMe (b), dnmBr (c), and dnmBrOMe (d).

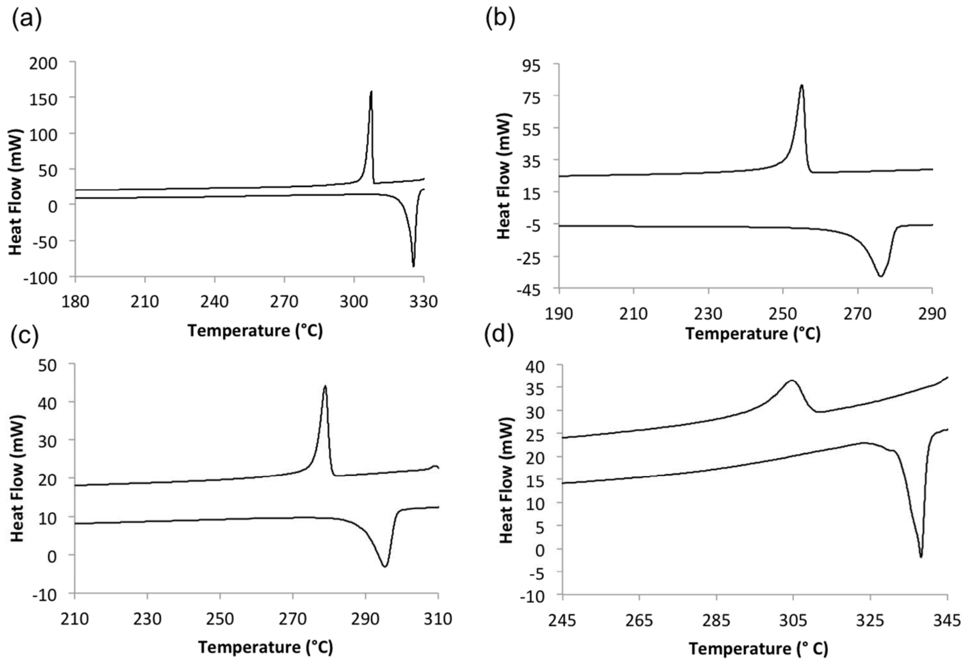

Fig. S17. DSC thermograms of BF_2dnm (a), BF_2dnmOMe (b), BF_2dnmBr (c), and BF_2dnmBrOMe (d).

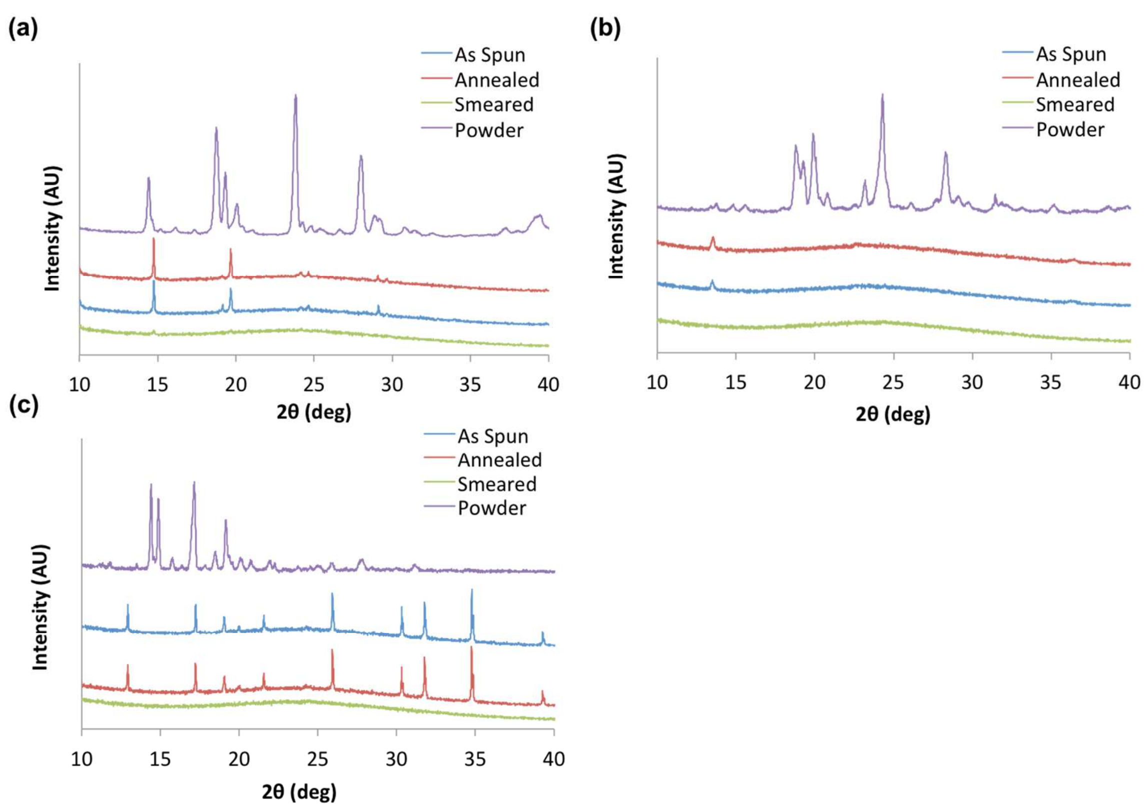

Fig. S18. Powder XRD patterns of dnm (a), dnmBr (b), dnmBrOMe (c) as pristine powders and AS, TA, and SM thin films.

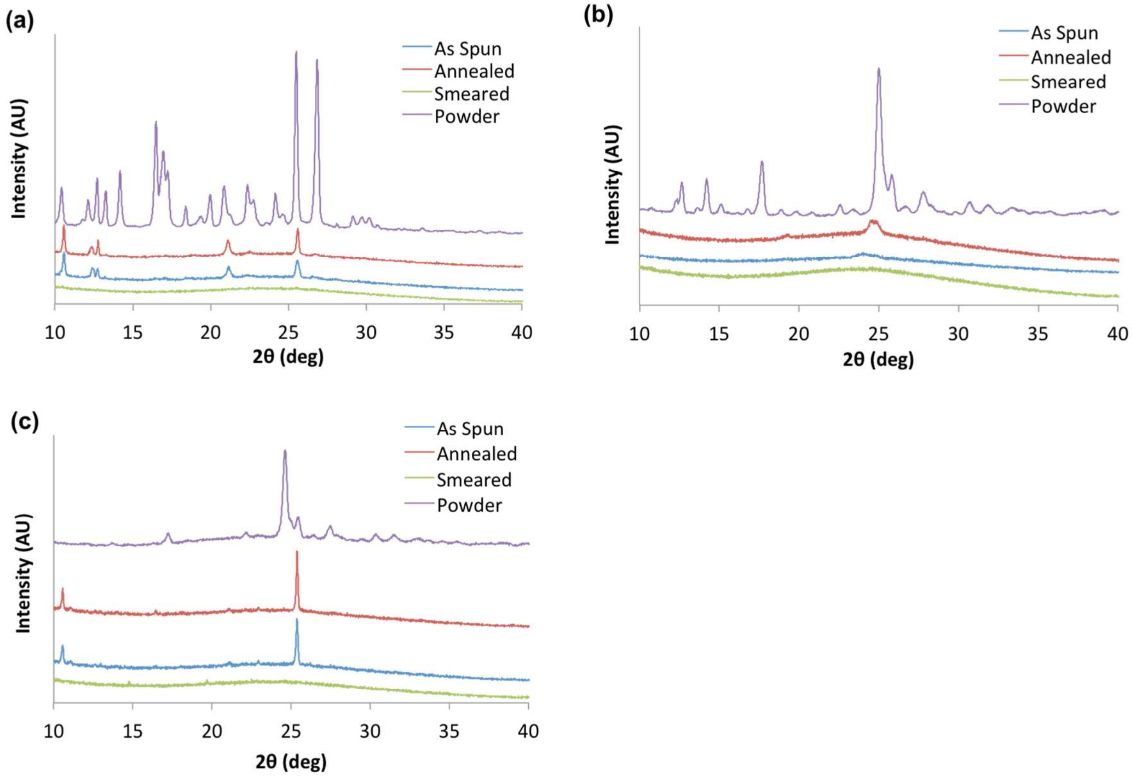

Fig S19. Powder XRD patterns of BF_2dnm (a), BF_2dnmBr (b), BF_2dnmBrOMe (c) as pristine powders and AS, TA, and SM thin-films.

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