Electronic Supplementary Information

Effects of the Benzoxazole Group on Green Fluorescent Protein Crystal Structure and Solid State Photophysics

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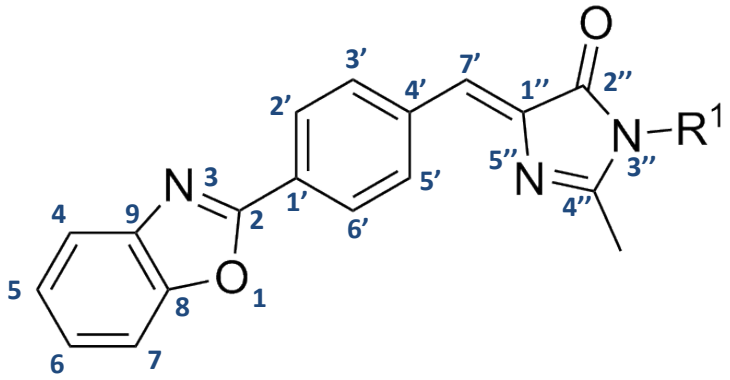


Figure S1. Numbering of the atoms for NMR characterization.

^{1}H NMR data of N-[4-(1,3-benzoxazol-2-yl)phenyl]methylidene-alkylamines

N-[4-(1,3-benzoxazol-2-yl)phenyl]methylidene-methylamine (5).

^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.34 (s, 1H, N=CH), 8.28 (d, ^3J = 9 Hz, 2H, $H_{2'}$ and $H_{6'}$), 7.84 (d, ^3J = 9 Hz, 2H, $H_{3'}$ and $H_{5'}$), 7.76 (m, 1H, H_7), 7.58 (m, 1H, H_4), 7.34 (m, 2H, H_5 and H_6), 3.22 (s, 3H, CH_3).

N-[4-(1,3-benzoxazol-2-yl)phenyl]methylidenebutylamine (6)

^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.30 (s, 1H, N=CH), 8.28 (d, ^3J = 9 Hz, 2H, $H_{2'}$ and $H_{6'}$), 7.86 (d, ^3J = 9 Hz, 2H, $H_{3'}$ and $H_{5'}$), 7.75 (m, 1H, H_7), 7.58 (m, 1H, H_4), 7.34 (m, 2H, H_5 and H_6), 3.64 (t, ^3J = 7.3 Hz, 2H, N-CH_2), 1.64 (m, 2H, N-CH_2-C$\underline{H}_2$), 1.42 (m, 2H, C$\underline{H}_2$-CH_3), 1.00 (t, ^3J = 7.4 Hz, 3H, CH_3).

N-[4-(1,3-benzoxazol-2-yl)phenyl]methylidenepentylamine (7)

^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.32 (s, 1H, N=CH), 8.29 (d, ^3J = 9 Hz, 2H, $H_{2'}$ and $H_{6'}$), 7.86 (d, ^3J = 9 Hz, 2H, $H_{3'}$ and $H_{5'}$), 7.75 (m, 1H, H_7), 7.57 (m, 1H, H_4), 7.34 (m, 2H, H_5 and H_6), 3.63 (t, ^3J = 7.2 Hz, 2H, N-CH_2), 1.67 (m, 2H, N-CH_2-C$\underline{H}_2$), 1.36 (m, 4H, C$\underline{H}_2$-C$\underline{H}_2$-CH_3), 0.94 (t, ^3J = 7.2 Hz, 3H, CH_2-C$\underline{H}_3$).

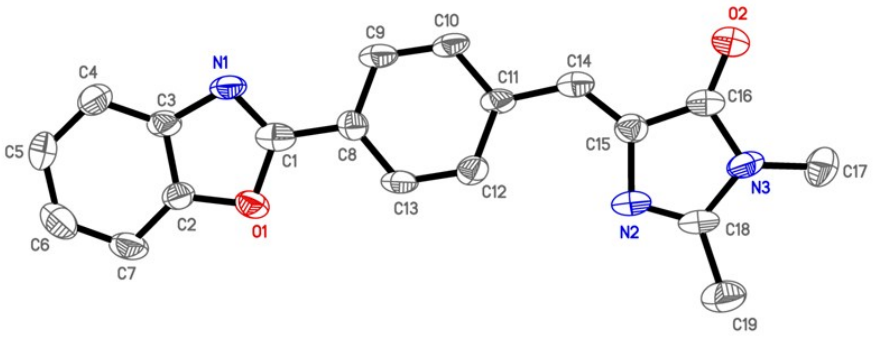
N-[4-(1,3-benzoxazol-2-yl)phenyl]methylidenedodecylamine (8)

^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.31 (s, 1H, N=CH), 8.29 (d, ^3J = 9 Hz, 2H, $H_{2'}$ and $H_{6'}$), 7.86 (d, ^3J = 9 Hz, 2H, $H_{3'}$ and $H_{5'}$), 7.76 (m, 1H, H_7), 7.57 (m, 1H, H_4), 7.35 (m, 2H, H_5 and H_6), 3.67 (t, ^3J = 7.3 Hz, 2H, N-CH_2), 1.67 (m, 2H, N-CH_2-C$\underline{H_2}$), 1.34 (m, 18H, CH_2), 0.91 (t, ^3J = 7.3 Hz, 3H, CH_3).

Crystallographic data

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{19}H_{15}N_3O_2$	$C_{22}H_{21}N_3O_2$	$C_{23}H_{23}N_3O_2$	$C_{30}H_{37}N_3O_2$
Formula weight	317.34	359.42	373.44	471.63
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ \bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions				
a (Å)	7.558(2)	4.6778(5)	7.4065(3)	25.4404(9)
b (Å)	13.561(3)	34.671(4)	22.5576(7)	7.3304(3)
c (Å)	14.948(4)	11.6713(16)	12.0964(4)	13.9803(4)
α (°)	88.586(11)	90	90	90
β (°)	88.421(12)	101.338(6)	95.776(2)	98.0030(10)
γ (°)	89.548(11)	90	90	90
Volume (Å^3)	1531.0(7)	1856.0(4)	2010.72(12)	2581.77(16)
Z	4	4	4	4
Crystal size (mm^3)	0.35 × 0.04 × 0.03	0.60 × 0.03 × 0.02	0.20 × 0.15 × 0.12	0.28 × 0.18 × 0.05
Reflections collected	23625	29993	46734	31912
Independent reflections	4959	3626	8283	4855
R_{int}	0.2019	0.1354	0.0529	0.0432
Parameters/Restraints	437/0	247/0	256/0	319/12
Final R_1 indice I>2σ(I)	0.1283	0.0562	0.0545	0.0396
$wR2$ all data	0.3620	0.1517	0.1570	0.0961
Largest diff. peak and hole (e.Å^{-3})	0.549 and -0.415	0.302 and -0.215	0.277 and -0.191	0.154 and -0.169
CCDC	1431493	1431494	1431495	1431496

Table S1. Crystal data of compounds **1**-**4**.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C16
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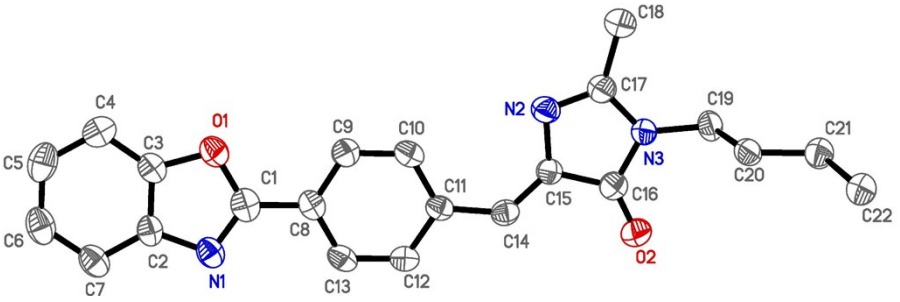
C13
C2
O1
N2
C18
C6
C7
C19

1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C2
O2
C7
N1
C13
C12

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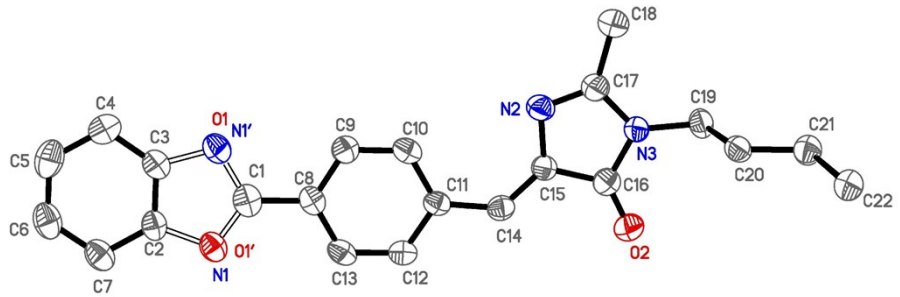
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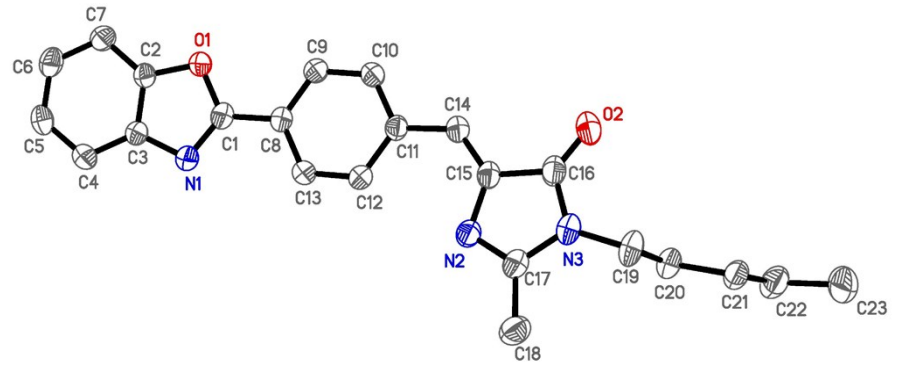
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C18

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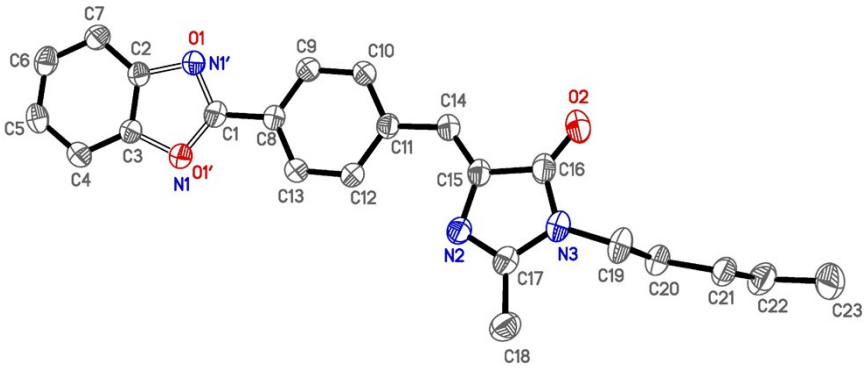
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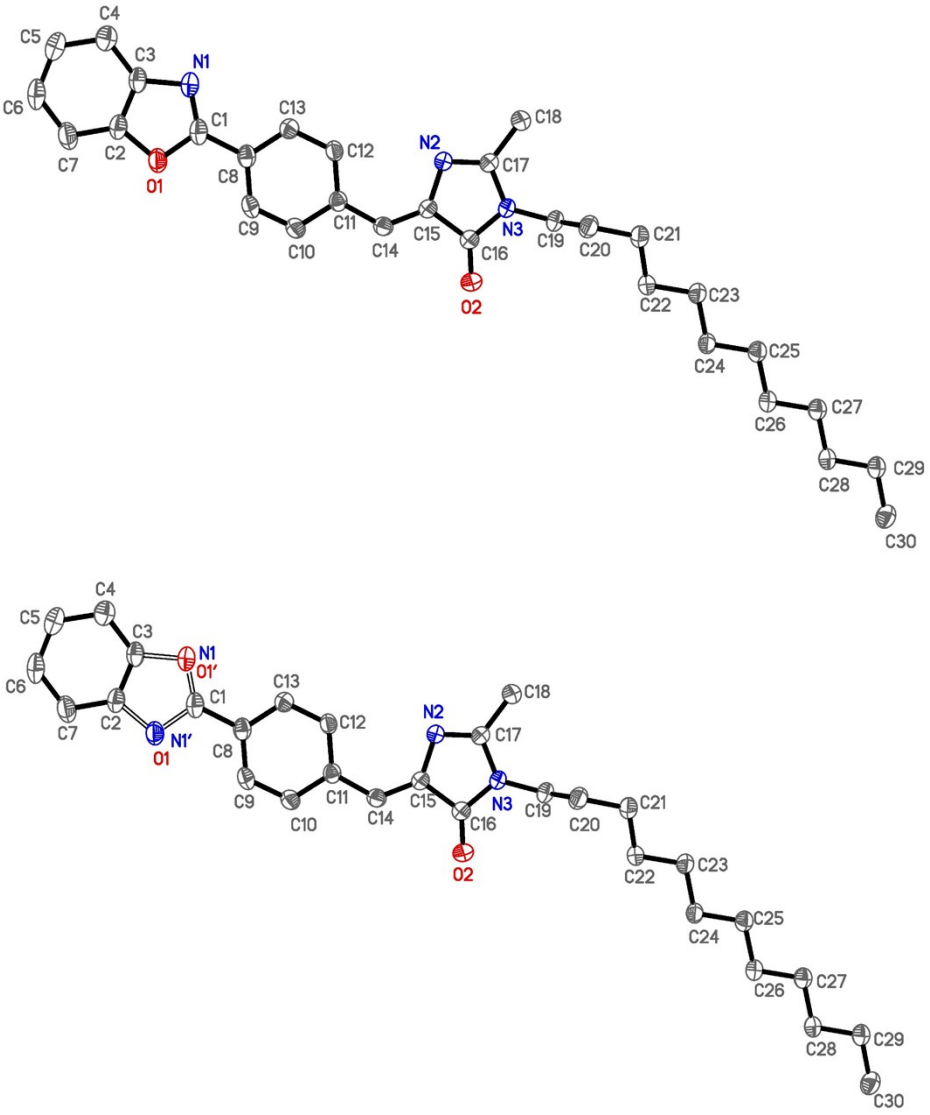


Figure S2. Molecular views of compounds **1**-**4**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

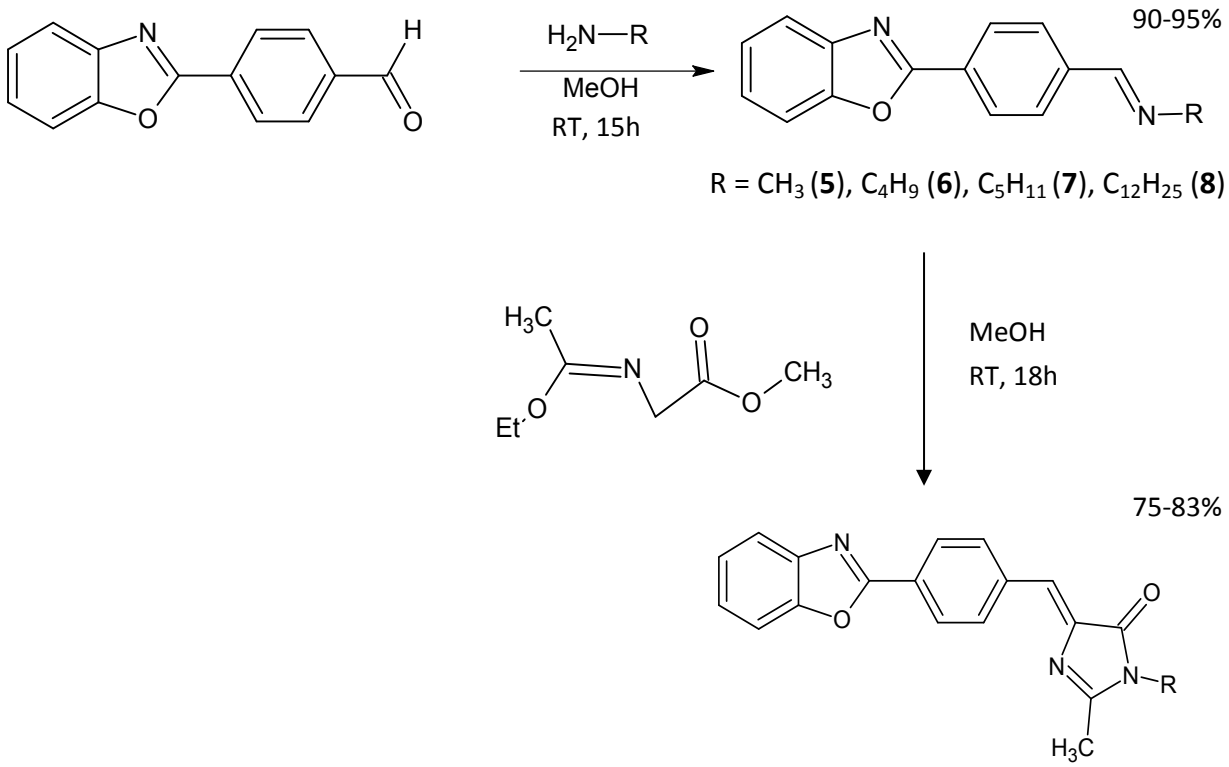


Figure S3. Scheme of synthesis.

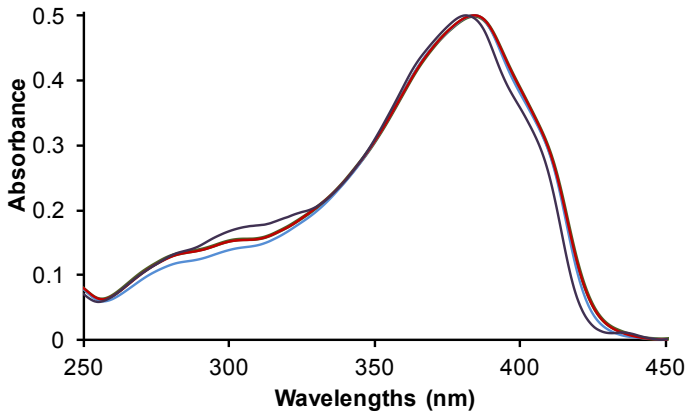


Figure S4. UV-vis absorption spectra of compounds **1** (purple line), **2** (red line), **3** (blue line), and **4** (green line) in ethanol. Dye concentration around 1.3×10^{-5} M. Absorption maximum was 382 nm for **1** and 384 for the other compounds.

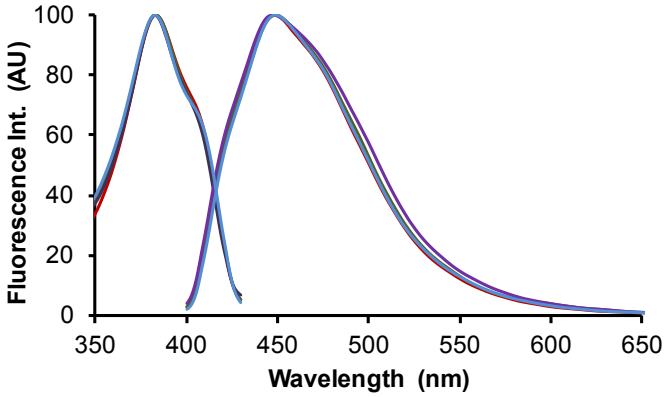


Figure S5. Normalized excitation (λ_{em} = 446 nm) and emission (λ_{ex} = 384 nm) spectra of compounds **1** (purple line), **2** (red line), **3** (blue line), and **4** (green line) in ethanol. Dye concentration around 1.3×10^{-6} M.

	Solid state	
Compound	λ_{em} (nm)	Φ_P
1	450-490, 612	$<10^{-3}$
2	620	0.18
3	616	0.16
4	612	0.26

Table S2. Solid-state spectroscopic characteristics of compounds **1-4**. Maximum emission wavelength (λ_{em}) and photoluminescence quantum yields (Φ_P). Excitation at 384 nm.

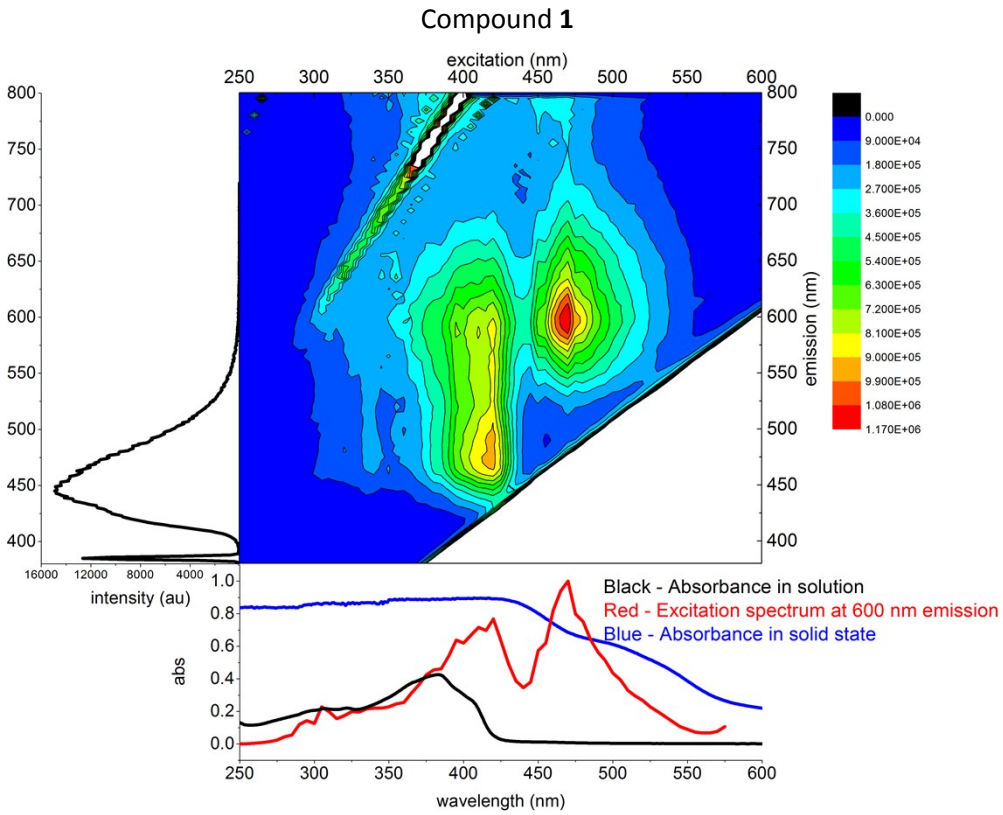


Figure S6: Steady-state fluorescence (left) and absorbance (bottom, black) spectra for **1** in solution. Also shown are the absorbance in the solid state (bottom, blue), the 3D solid state spectrum (center), and the excitation spectrum at 600 nm emission extracted from the 3D plot (bottom, red).

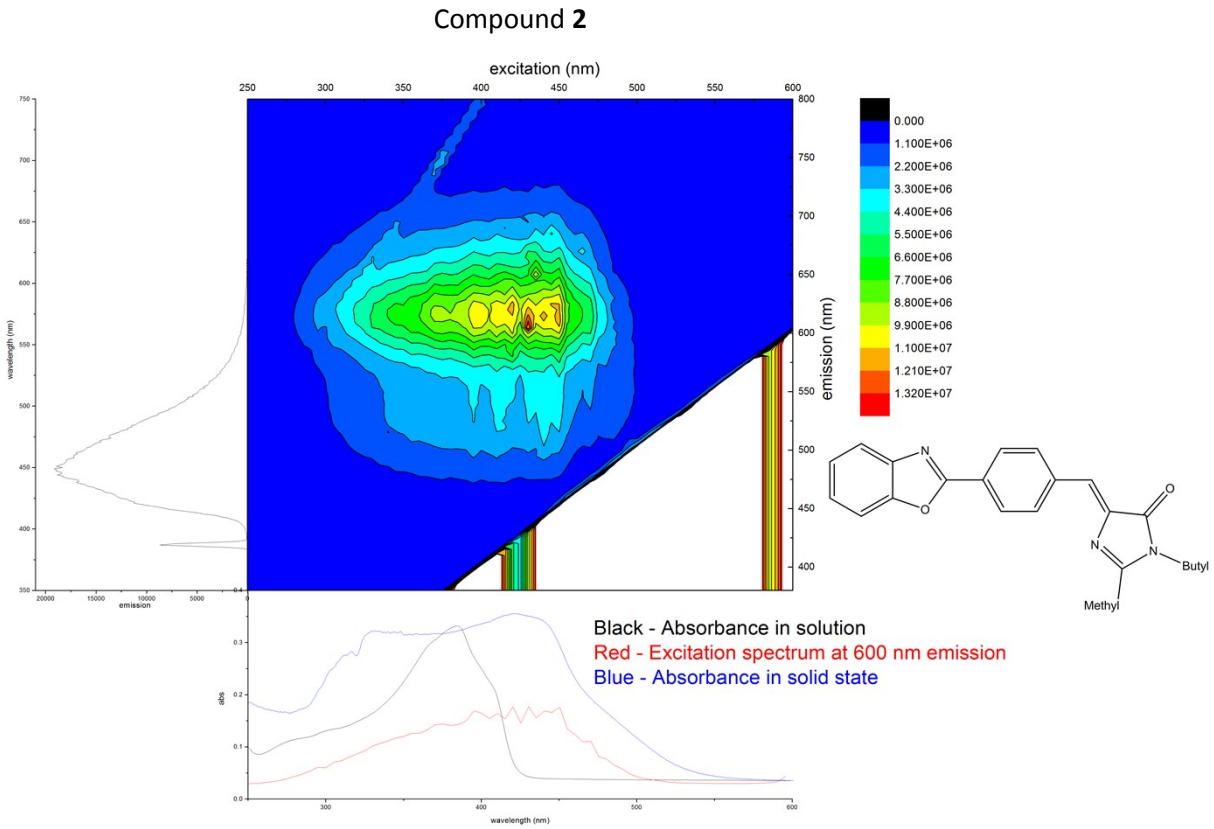


Figure S7: Steady-state fluorescence (left) and absorbance (bottom, black) spectra for **2** in solution. Also shown are the absorbance in the solid state (bottom, blue), the 3D solid state spectrum (center), and the excitation spectrum at 600 nm emission extracted from the 3D plot (bottom, red).

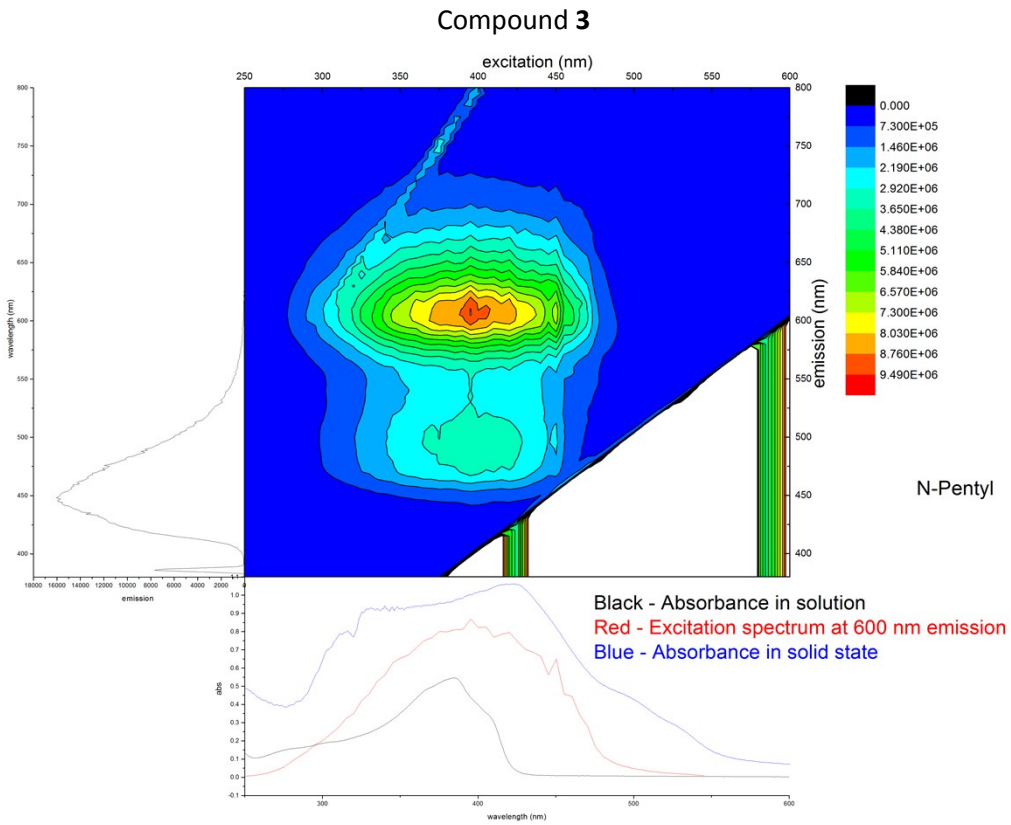


Figure S8: Steady-state fluorescence (left) and absorbance (bottom, black) spectra for **3** in solution. Also shown are the absorbance in the solid state (bottom, blue), the 3D solid state spectrum (center), and the excitation spectrum at 600 nm emission extracted from the 3D plot (bottom, red).

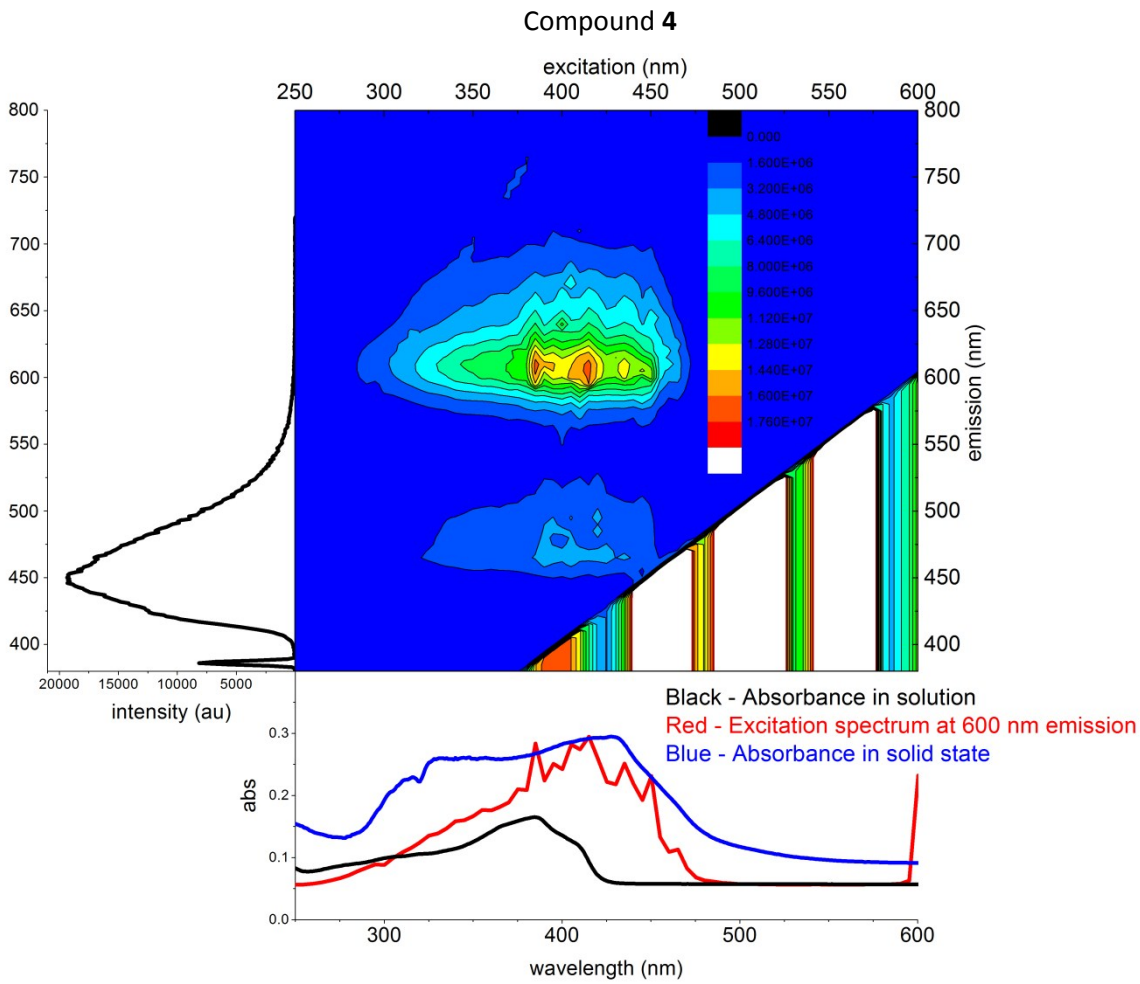


Figure S9: Steady-state fluorescence (left) and absorbance (bottom, black) spectra for **4** in solution. Also shown are the absorbance in the solid state (bottom, blue), the 3D solid state spectrum (center), and the excitation spectrum at 600 nm emission extracted from the 3D plot (bottom, red).

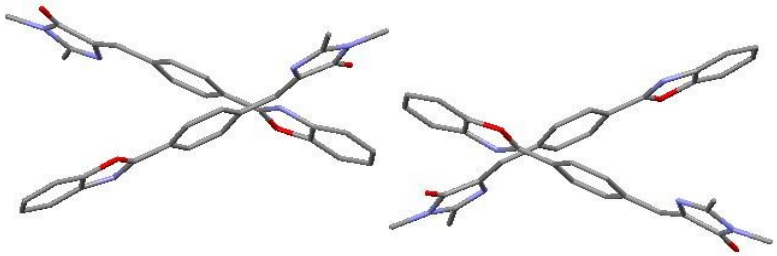
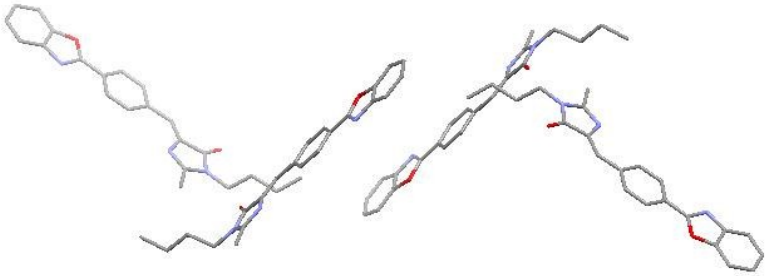
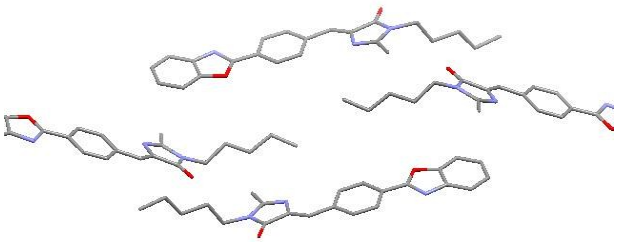
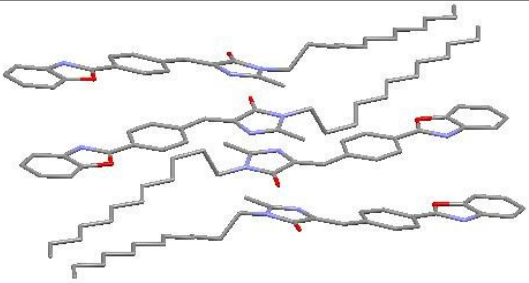
Compounds	Crystal cell
1	
2	
3	
4	

Figure S10. Molecular arrangement in the crystal cell for compounds **1** to **4**.