### SUPPORTING INFORMATION FOR:

# Rigidity and Polarity Effects on the Electronic Properties of Two Deep Blue Delayed Fluorescence Emitters

Christian M. Legaspi<sup>1</sup>, Regan E. Stubbs<sup>1</sup>, Md. Wahadoszaman<sup>2</sup>, David J. Yaron<sup>1</sup>, and Linda A. Peteanu<sup>1,\*</sup> <sup>1</sup>Department of Chemistry, Carnegie Mellon University <sup>2</sup>Department of Physics, University of Dhaka

> Abraham Kemboi and Eric Fossum Department of Chemistry, Wright State University

> Yongli Lu, Qi Zheng, and Lewis J. Rothberg Department of Chemistry, University of Rochester

### Section S1: Delayed emission in BOX/BTZ-CBZ compounds



**Figure S1** Prompt and delayed emission measurements for (a) BOX-CBZ and (b) BTZ-CBZ in toluene at room temperature. Emission dynamics for both compounds at room temperature (c) in air and (d) under argon.

# Section S2: Linear fitting for scaling calculated $\Delta E_{ST}$

For the Van Voorhis method, "Protocol C" was used.<sup>1</sup> The SI for Ref. 1 gave values of calculated and measured  $\Delta E_{ST}$ . Linear least squares yielded:

 $\Delta E_{ST}^{expt} = 1.2468 \, \Delta E_{ST}^{calc}. \tag{1}$ 

For the Aspuru-Guzik method, the data for calculated and measured  $\Delta E_{ST}$  were not provided explicity.<sup>2</sup> The fit line in Ref. 2 was calculated to be approximately

 $\Delta E_{ST}^{expt} = 0.5224 \, \Delta E_{ST}^{calc}. \tag{2}$ 

# Section 3: TD-DFT results for BOX-CBZ and BTZ-CBZ

The HOMO and LUMO correspond to MO 102 and 103 in BOX-CBZ, and MO 106 and 107 in BTZ-CBZ, respectively.

State	<sup>a</sup> Energy	Ъλ	<sup>c</sup> f	<sup>d</sup> MO Transition	<sup>e</sup> Cl Coeff.
1	4.0803	303.86	0.1925	100→103	-0.13636
				102→103	0.64362
				102→105	-0.17567
2	4.3785	283.17	0.0688	101→108	0.20619
				102→104	0.66080
3	4.7677	260.05	0.7781	100→103	0.66235
				101→103	0.10716
				102→103	0.12431
4	4.8545	255.40	0.0125	100→103	-0.10229
				101→103	0.67609
				101→105	-0.13148
5	4.8904	253.53	0.1656	99→104	-0.10704
				101→104	0.62398
				102→108	-0.25407
				102→110	0.10392

Table S1: Gas-phase TD-DFT properties of the lowest 5 excited singlet states of BOX-CBZ

<sup>*a*</sup>Vertical excitation energy in eV. <sup>*b*</sup>Excitation wavelength in nm. <sup>*c*</sup>Oscillator strength. <sup>*d*</sup>Major molecular orbital contributions to the transition (where CI coeff. magnitude > 0.1). <sup>*e*</sup>CI coefficients for the MO contributions.

State	<sup>a</sup> Energy	<sup>b</sup> λ	<sup>c</sup> f	dMO	<sup>e</sup> Cl Coeff
				Transition	ci coeff.
1	3.9472	314.11	0.1077	103→107	-0.16241
				104→107	-0.12062
				106→107	0.64449
				106→109	-0.10056
2	4.3790	283.14	0.0899	105→112	0.20452
				106→108	0.65673
3	4.6287	267.86	0.5657	104→107	0.65797
				106→109	-0.15619
4	4.6862	264.57	0.4590	104→107	0.13354
				106→107	0.10868
				106→109	0.64850
				106→111	0.14931
5	4.7597	260.49	0.0054	105→107	0.69122

Table S2: Gas-phase TD-DFT properties of the lowest 5 excited singlet states of BTZ-CBZ

<sup>a</sup>Vertical excitation energy in eV. <sup>b</sup>Excitation wavelength in nm. <sup>c</sup>Oscillator strength. <sup>d</sup>Major molecular orbital contributions to the transition (where CI coeff. magnitude > 0.1). <sup>e</sup>CI coefficients for the MO contributions.

## Section 4: Stark spectroscopy fitting coefficients and calculated $\Delta \alpha$

 $\Delta \alpha$  is calculated by

$$\Delta \alpha = 2ahcB_{\chi} \tag{3}$$

where a is  $10^{-2}$  m/cm, h is Planck's constant, c is the speed of light, and  $B_{\chi}$  is the linear fitting coefficient for the first derivative contribution. Values of  $\Delta \alpha$  are given in cubic Angstroms.

Sample	<sup>a</sup> Expt.	<sup>b</sup> Group	$^{c}\Delta \alpha$	${}^{d}A_{\chi}$	${}^{e}B_{\chi}$	${}^{f}C_{\chi}$
BOX-CBZ	EA	G1	-15	6.08 x 10 <sup>-15</sup>	-3.81 x 10 <sup>-13</sup>	1.29 x 10 <sup>-8</sup>
		G2/G3	-24	-5.90 x 10 <sup>-15</sup>	-6.76 x 10 <sup>-13</sup>	2.77 x 10 <sup>-10</sup>
		G4/G5	212	1.14 x 10 <sup>-14</sup>	5.82 x 10 <sup>-12</sup>	1.82 x 10 <sup>-9</sup>
	EF		-37	3.38 x 10 <sup>-16</sup>	-1.06 x 10 <sup>-12</sup>	7.24 x 10 <sup>-9</sup>
BTZ-CBZ	EA	G1/G2	219	-2.29 x 10 <sup>-15</sup>	6.13 x 10 <sup>-12</sup>	2.38 x 10 <sup>-8</sup>
		G3/G4	-61	1.92 x 10 <sup>-16</sup>	-1.70 x 10 <sup>-12</sup>	3.26 x 10 <sup>-9</sup>
	EF	G1/G2	-1042	1.87 x 10 <sup>-14</sup>	-2.92 x 10 <sup>-11</sup>	2.63 x 10 <sup>-8</sup>
		G3/G4	-598	-9.01 x 10 <sup>-9</sup>	-1.68 x 10 <sup>-11</sup>	5.70 x 10 <sup>-9</sup>

<sup>*a*</sup>Experiment type. <sup>*b*</sup>Grouping of Gaussians for shown parameters for fits done to more than one parameter set. <sup>*c*</sup>Average change in polarizability in Å<sup>3</sup>. <sup>*d*</sup>Zeroth derivative fitting component. <sup>*e*</sup>First derivative fitting component. <sup>*f*</sup>Second derivative fitting component.

#### Section 5: Lippert-Mataga solvatochromism analysis

The Lippert-Mataga solvent polarity model<sup>3-6</sup> was used to calculate  $|\Delta \mu|$  (eq. 4) which assumes that the value is the same in absorption and emission:

$$\Delta \nu = \Delta \nu_0 - \left(\frac{2|\Delta \mu|^2}{hca^3}\right) \Delta f \tag{4}$$

where  $\Delta v$  is the observed Stokes shift in wavenumbers,  $\Delta v_0$  is the Stokes shift in the absence of solvent, and a is the Onsager radius.  $\Delta f$  is the orientation polarizability of the solvent:

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{5}$$

where  $\epsilon$  and n are the solvent dielectric constant and refractive index, respectively. The Onsager radius was calculated on the ground-state electron density of the molecules by the same density functional theory methods employed in the main manuscript using the Gaussian09 software package.<sup>7</sup>

Because the absorption spectra for BOX-CBZ and BTZ-CBZ do not possess mirror symmetry and contain many overlapping bands, it is difficult to locate the exact maximum of the CT absorption band. Instead, the maximum of the excitation spectrum in the CT absorption region was used.

Using an Onsager radius of 5.63 Å (BOX-CBZ) and 5.71 Å (BTZ-CBZ) the model predicts  $|\Delta \mu|$  to be 16.5 D and 17.1 D, respectively.



Figure S2: Lippert-Mataga Analysis of BOX-CBZ and BTZ-CBZ in 11 solvents (listed in Table S4).

Solvent	$^{a}\epsilon$	<sup>b</sup> n	$^{c}\Delta f$
cyclohexane	2.0243	1.4235	-0.0002
methylcyclohexane	2.024	1.4231	-0.0001
isopentane	1.845	1.3537	0.0017
toluene	2.379	1.4941	0.0140
1,4-dioxane	2.2189	1.4224	0.0214
chloroform	4.8069	1.4890	0.1347
2-methyltetrahydrofuran	6.97	1.4059	0.2024
tetrahydrofuran	7.52	1.4050	0.2096
N-methyl-2-pyrrolidone	32.55	1.4684	0.2597
acetonitrile	36.64	1.3422	0.3049
methanol	33.0	1.3288	0.3086

Table S4. Solvent properties for Lippert-Mataga analysis.

<sup>a</sup>Dielectric constant. <sup>b</sup>Refractive index. <sup>c</sup>Orientational polarizability.

# Section 6: Absorption of BOX-CBZ and BTZ-CBZ in various solvents



**Figure S3.** Absorbance of (a) BOX-CBZ and (b) BTZ-CBZ in multiple solvents. Solvent abbreviations: methylcyclohexane (MCH), toluene (TOL), 1,4-dioxane (DXN), chloroform (CFM), tetrahydrofuran (THF), acetonitrile (ACN)

# Section 7: Derivation of oscillator strength equation from experimental parameters

Derivation of eq. 11 (here as eq. 6):

$$f = \left(\frac{m\epsilon_0 c^3 h^2}{2\pi e^2}\right) \frac{\Phi}{\tau_f E_{\text{em}}^2} \tag{6}$$

Beginning with eqn. 7, derived by Hilborn<sup>9</sup>:

$$f = \frac{2\pi m \epsilon_0 c^3}{e^2} \frac{g_2}{g_1} \frac{1}{\omega^2} A_{21}$$
(7)

where f is oscillator strength,  $\epsilon_0$  is vacuum permittivity, m is the electron mass, c is the speed of light,  $\omega$  is the transition frequency in rad/s, e is the electron charge,  $\frac{g_2}{g_1}$  is the ratio of upper states to lower states (taken as 1 here), and A<sub>21</sub> is the Einstein coefficient for the rate of spontaneous emission. All quantities are in SI units, unless otherwise noted. Converting  $\omega$  to E<sub>em</sub> in SI units gives

$$f = \frac{m\epsilon_0 c^3 h^2}{2\pi e^2} \frac{1}{E_{em}^2} A_{21}$$
(8)

 $A_{21}$  is =the change in the population of molecules in the excited state per time,

$$-\frac{dn_2}{dt} = A_{21}n_2 = k_r n_2 \tag{9}$$

where  $n_2$  is the number of molecules in the excited state and  $k_r$  is the radiative rate. Logically,  $A_{21} = k_r$  follows from this. The quantum yield ( $\Phi$ ) is

$$\Phi = \frac{k_r}{k_r + k_{nr}} \tag{10}$$

where  $k_{nr}$  is the rate of non-radiative decay. The fluorescence lifetime  $(\tau_f)$  is  $\tau_f = \frac{1}{k_r + k_{nr}}$  (11)

Combining eqs. 8, 10, 11 and the relation  $A_{21} = k_r$ , eq. 6 naturally follows.

# References

(1) Hait, D.; Zhu, T.; McMahon, D. P.; Van Voorhis, T. Prediction of Excited-State Energies and Singlet–Triplet Gaps of Charge-Transfer States Using a Restricted Open-Shell Kohn–Sham Approach. *J. Chem. Theory Comput.* **2016**, *12*, 3353-3359.

(2) Gómez-Bombarelli, R.; Aguilera-Iparraguirre, J.; Hirzel, T. D.; Duvenaud, D.; Maclaurin, D.; Blood-Forsythe, M. A.; Chael, H. S.; Einzinger, M.; Ha, D.-G.; Kim, S., *et al.* Design of Efficient Molecular Organic Light-Emitting Diodes by a High-Throughput Virtual Screening and Experimental Approach. *Nat. Mater.* **2016**, *15*, 1120-1128.

(3) Lippert, E. Z. Solvation Theory. *Z. Naturforsch. A* **1955**, *10*, 541-545.

(4) Mataga, N.; Kaifu, Y.; Koizumi, M. Solvent Effects Upon Fluorescence Spectra and the Dipole Moments of Excited Molecules. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465-470.

(5) Ghoneim, N.; Rohner, Y.; Suppan, P. Solvatochromic and Thermochromic Effects in Low-Temperature Rigid Matrices. *Faraday Discuss. Chem. Soc.* **1988**, *86*, 295-308.

(6) Lakowicz, J. *Principles of Fluorescence Spectroscopy*; Springer, US: Boston, MA, 2006.

(7) *Gaussian09, Revision D. 01*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A., et al., Wallingford CT 2016.

(8) *CRC Handbook of Chemistry and Physics* Haynes, W., Ed.; CRC Press: Boca Raton, FL, 2016.

(9) Hilborn, R. C. Einstein Coefficients, Cross Sections, *f* Values, Dipole Moments, and All That. *Am. J. Phys.* **1982**, *50*, 982-986.