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A simple method for calibration of hybrid exchange–correlation functionals for precise calculations of fluorescence wavelengths of dibenzoylmethanatoboron difluoride exciplexes with benzene, alkylbenzenes and pyridine

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CALCULATION PROCEDURE

Quantum chemistry calculations were performed using the density functional theory (DFT) for the ground states and time-dependent DFT (TDDFT) for the excited states, implemented in the ORCA 5.0 software package.[S1–S3] We choose the conventional hybrid GGA BHHLYP (BHANDHLYP, HFX = 0.5) exchange-correlation functional. It has demonstrated satisfactory results in calculations of charge-transfer systems according to the published data[S4, S5] and our calculations.[S6] Ahlrichs's double-zeta def2-SVP[S7] and triple-zeta TZVP basis sets,[S8] including polarization functions, were used. Grimme's dispersion correction within the Becke–Johnson damping[S9,S10] and solvent (hexane, benzene, alkylbenzene) effects within the CPCM model[S11] for some models were also taken into account .

The calculation procedure included two steps: firstly, we optimized the geometry of the systems with the def2-SVP basis set; secondly we calculated energy characteristics of the studied systems using the def2-TZVP basis set with the geometries optimized with the def2-SVP basis set. In this approach, the time of calculations could be significantly reduced while maintaining the high accuracy of the calculated total energies.

The ORCA 5.0 software package used in the calculations allows the variation of internal parameters of the incorporated density functionals. The total exchange-correlation energy E_{XC} for hybrid density functionals is given by the equation:[S12]

$$E_{XC} = aE_{HF}^{X} + (1-a)E_{LSD}^{X} + bE_{GGA}^{X} + E_{LSD}^{C} + cE_{GGA}^{C},$$

where E_{HF}^{X} is the Hartree-Fock exchange energy, E_{LSD}^{X} is the local (Slater) exchange energy, E_{GGA}^{X} is the gradient correction to the exchange energy, E_{LSD}^{C} is the local energy correction based on spin density, E_{GGA}^{C} is the gradient correction to the correlation energy, a, b and c are the parametrization parameters.

For one-parameter hybrid density functionals (BHHLYP in particular), the exchange-correlation energy has a simple form:

$$E_{XC} = aE_{HF}^{X} + (1-a)E_{DFT}^{X} + E_{DFT}^{C},$$

where a and (1 – a) specify the fractions of the Hartree-Fock and DFT exchange energies.

Table S1. Fluorescence wavelengths λ, transition energies *E*, and charge-transfer (CT) parameters of $DBMBF_2$ exciplexes with alkylbenzenes and pyridine calculated with different values of parameter HFX and corresponding experimental data.[S13,S14] Values in brackets are calculated with solvent effect within CPCM

	Benzene			Toluene			*p*-Xylene		
XHF	λ, nm	*E*, Ev	CT	λ, nm	*E*, Ev	CT	λ, nm	*E*, Ev	CT
0.30	447	2.77	0.83						
0.31	443	2.80							
0.32	438	2.83	0.79						
0.33	434(434)	2.85(2.86)	0.77(0.58)						
0.34	431(431)	2.87(2.88)	(0.57)						
0.35	427	2.90	0.73	545	2.28	0.900			
0.36	424	2.92	0.70						
0.37	421	2.95	0.68						
0.38	418	2.96	0.66						
0.39	416	2.98							
0.40	413(416)	3.00(2.98)	0.62(0.48)	492	2.52	0.870			
0.41	410(413)	3.03(3.00)	0.59(0.47)	485	2.56	0.867			
0.42	407	3.04	0.57	479(437)	2.59(2.83)	0.864(0.691)			
0.43	405	3.06	0.56	454(434)	2.73(2.86)	0.844(0.680)	496	2.50	
0.44				(431)	(2.88)	(0.667)			
0.45				442	2.81	0.824	492	2.52	0.884
0.46				438	2.83	0.819	486	2.55	0.881
0.47				432(421)	2.87(2.94)	0.802(0.625)	480(457)	2.58(2.71)	0.877(0.765)
0.48				423	2.93		474(453)	2.62(2.74)	0.873(0.755)
0.49							469(449)	2.65(2.76)	0.869 (0.744)
0.50	391	3.17	0.45	419	2.96	0.763	464(446)	2.67(2.78)	0.866(0.734)
0.51							459	2.70	0.862
0.52							453	2.74	0.855
0.53							448(435)	2.77(2.85)	0.848(0.699)
0.54							443	2.80	0.839
Ref [S13]	427	2.90		444	2.79		470	2.64	
Ref [S14]		3.00			2.89			2.77	

	Trimethylbenzene			Isodurene			Pyridine		
XHF	λ, nm	*E*, Ev	CT	λ, nm	*E*, Ev	CT	λ, nm	*E*, Ev	CT
0.37									
0.38							(422)	(2.94)	(0.475)
0.39							(420)	(2.95)	(0.460)
0.4							(417)	(2.97)	(0.447)
0.41									
0.42									
0.43							421(411)	2.95(3.02)	0.591(0.406)
0.44							418(408)	2.96(3.04)	0.575(0.397)
0.45	507	2,44	0,857	539	2,30	0,873	415(406)	2.99(3.05)	0.556(0.388)
0.46	(473)	(2.62)	(0.801)	(501)	(2.48)	(0.871)	404(395)	3.07(3.14)	0.493(0.335)
0.47	(469)	(2.64)	(0.793)	(496)	(2.50)	(0.867)	393(384)	3.15(3.23)	0.439(0.289)
0.48	(465)	(2.67)	(0.781)	(490)	(2.53)	(0.863)			
0.49	478	2.59	0.832	(484)	(2.56)	(0.860)			
0.5	473	2.62	0.827	505	2.46	0.861	436	2.84	0.745
0.51	469(455)	2.64(2.73)	0.818	499	2.48	0.859	432	2.87	0.736
0.52	465	2.67	0.81	494	2.51	0.856	429	2.89	0.725
0.53				488(465)	2.54(2.67)	0.853(0.841)	426	2.91	0.714
0.54				482	2.57	0.849			
Ref [S13]	472	2.63		497	2.49				
Ref [S14]		2.64			2.54		418	2.96	

Table S2. Fluorescence wavelengths λ, transition energies E, and charge-transfer (CT) parameters of $DBMBF_2$ exciplexes with benzene calculated using BHHLYP and PBE0 functionals with different values of parameter HFX and corresponding experimental data.[S13]

Benzene	BHHLYP			PBE0		
XHF	λ, nm	*E*, Ev	CT	λ, nm	*E*, Ev	CT
0.25	565	2.19	0.93	466	2.66	0.83
0.34	431	2.87		429	2.89	0.66
0.35	427	2.90	0.73	430	2.89	0.66
0.36	424	2.92	0.70	424	2.93	0.63

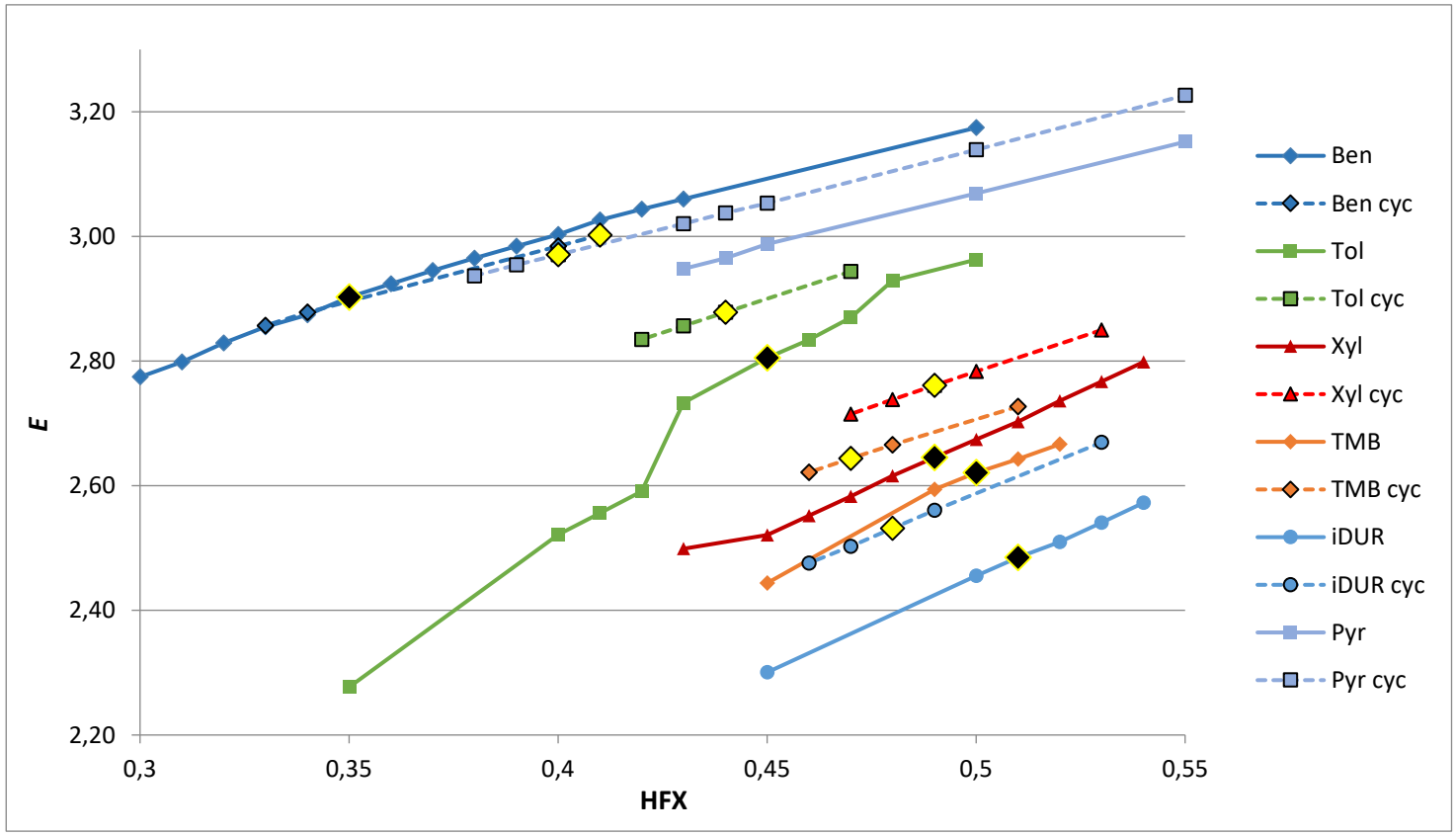

Figure S1. *E*(HFX) correlations for benzene (Ben), toluene (Tol), p-xylene (Xyl), trimethylbenzene (TMB), isodurene (iDUR), and pyridine (Pyr). Gas phase calculations are shown by solid lines. Calculations with CPCM are shown by dashed lines with framed points. Points corresponding to experimental data are shown by black (Ref [S13]) and yellow (Ref [S14]) diamonds.

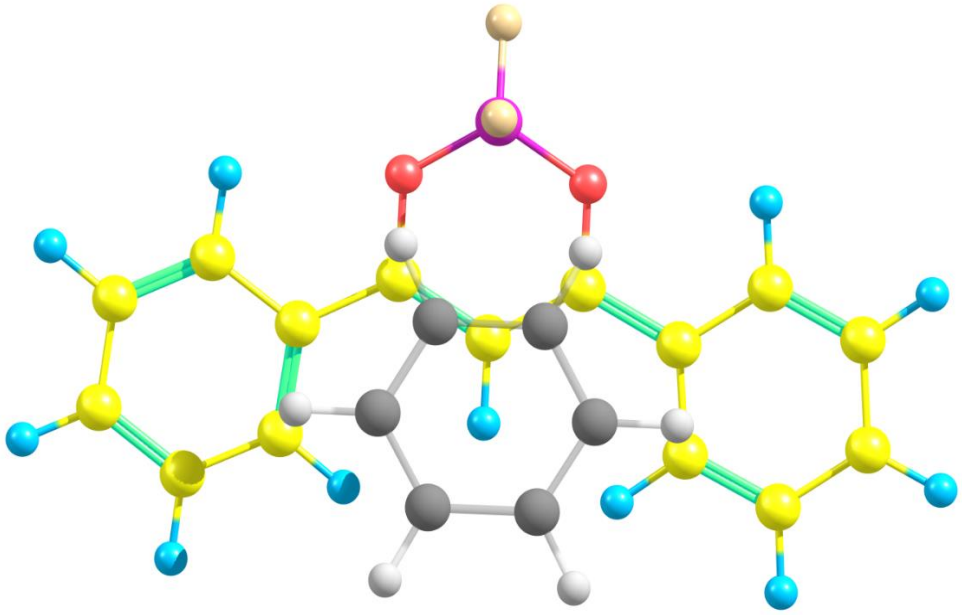

Figure S2. Optimized structure of $DBMBF_2$–benzene exciplex (HFX = 0.35).

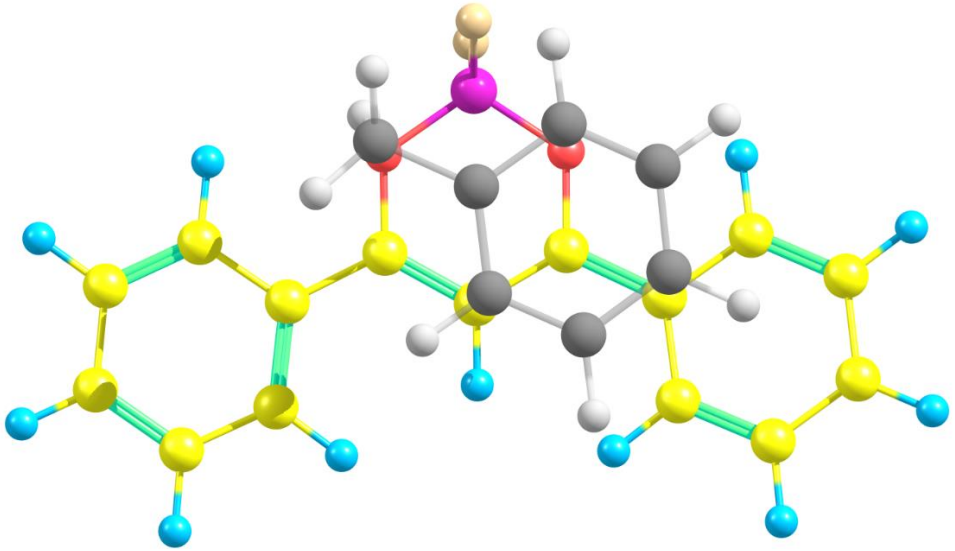

Figure S3. Optimized structure of $DBMBF_2$–toluene exciplex (HFX = 0.45).

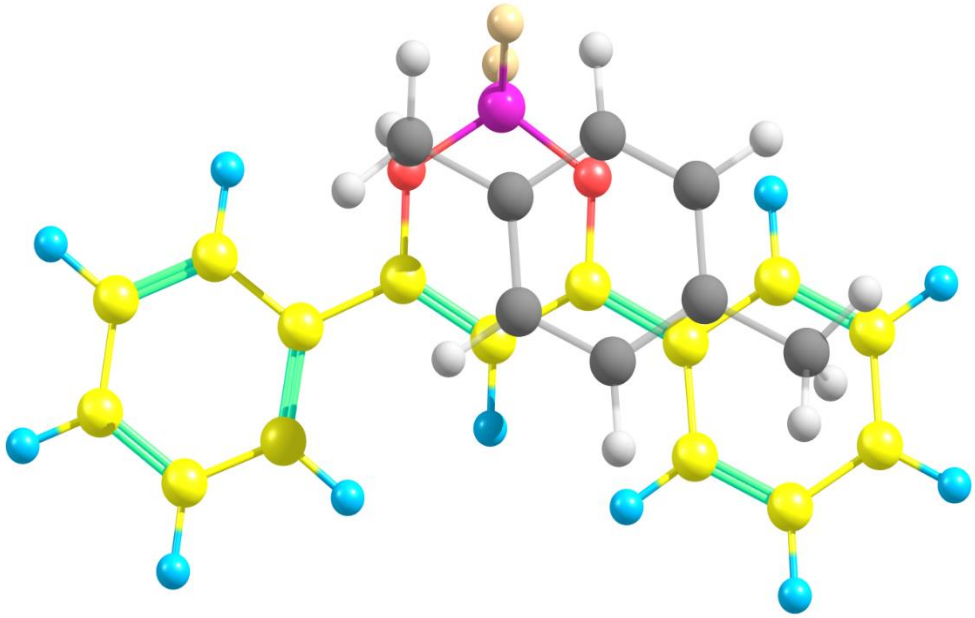

Figure S4. Optimized structure of $DBMBF_2$–*p*-xylene exciplex (HFX = 0.49).

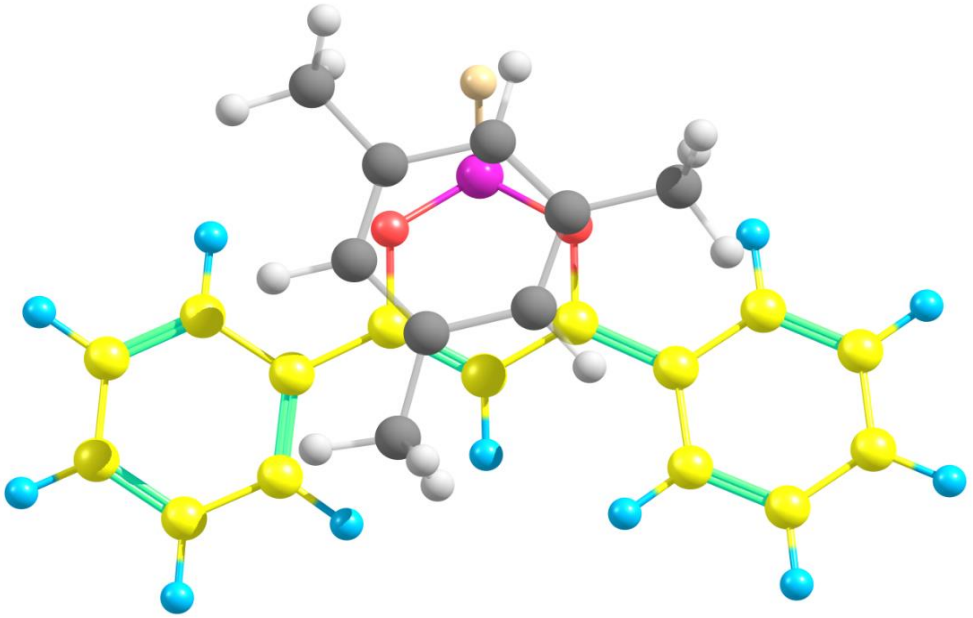

Figure S5. Optimized structure of $DBMBF_2$–1,3,5-trimethylbenzene exciplex (HFX = 0.50).

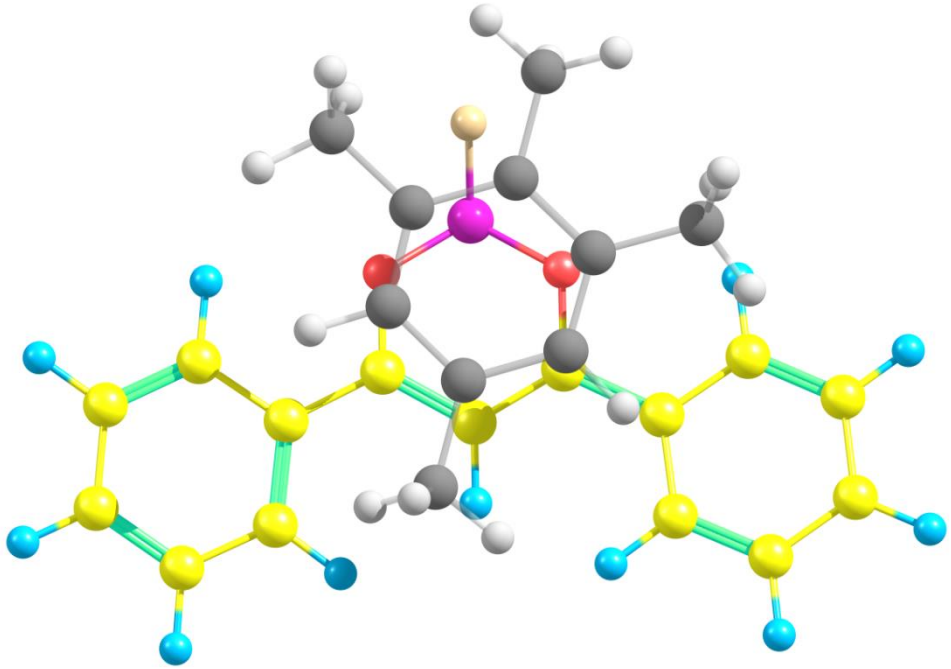

Figure S6. Optimized structure of $DBMBF_2$–*iso*-durene exciplex (HFX = 0.51).

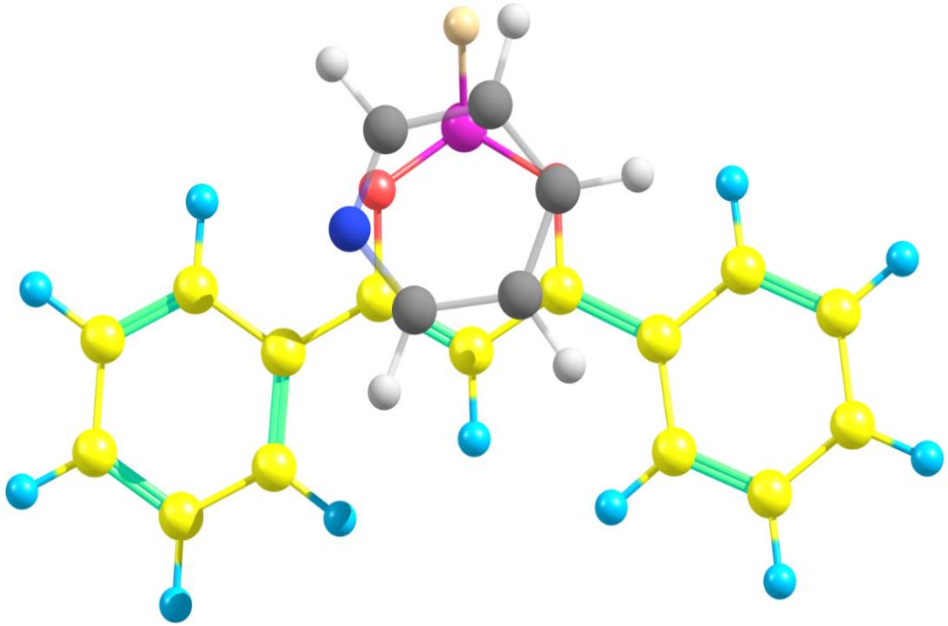

Figure S7. Optimized structure of $DBMBF_2$–pyridine exciplex (HFX = 0.44).

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