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SUPPORTING INFORMATION

FOR

Theoretical Exploitation of Acceptors Based on Benzobis(thiadiazole) and Derivatives for Organic NIR-II Fluorophores

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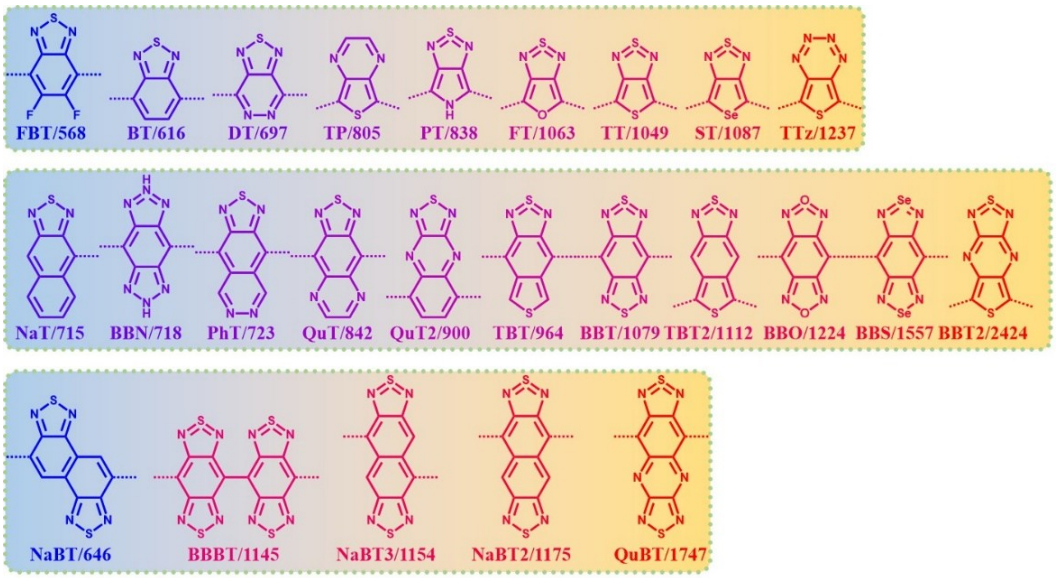

The acceptor abbreviations stand for BT = benzo[c][1,2,5]thiadiazole, FBT = 5,6-difluorobenzo[c][1,2,5]thiadiazole, DT = [1,2,5]thiadiazolo[3,4-d]pyridazine, PT = pyrrolo[3,4-c][1,2,5]thiadiazole, FT = furo[3,4-c][1,2,5]thiadiazole, TT = thieno[3,4-c][1,2,5]thiadiazole, ST = selenopheno[3,4-c][1,2,5]thiadiazole, TP = thieno[3,4-b]pyrazine, TTz = thieno[3,4-e][1,2,3,4]tetrazine, BBT = benzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole), BBT2 = [1,2,5]thiadiazolo[3,4-b]thieno[3,4-e]pyrazine, TBT2 = thieno[3',4':4,5]benzo[1,2-c][1,2,5]thiadiazole, NaT = naphtho[2,3-c][1,2,5]thiadiazole, PhT = [1,2,5]thiadiazolo[3,4-g]phthalazine, QuT = [1,2,5]thiadiazolo[3,4-g]quinoxaline, QuT2 = thieno[3,4-b]quinoxaline, BBN = 2H-benzo[1,2-d:4,5-d']bis([1,2,3]triazole)-6-ium-5-ide, BBO = benzo[1,2-c:4,5-c']bis([1,2,5]oxadiazole), BBS = benzo[1,2-c:4,5-c']bis([1,2,5]selenadiazole), BBBT = bibenzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole), QuBT = bis([1,2,5]thiadiazolo)[3,4-b:3',4'-g]quinoxaline, NaBT = naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole), NaBT2, NaBT3 = naphtho[2,3-c:6,7-c']bis([1,2,5]thiadiazole).

Figure S1. Full names of 25 acceptors in this work.

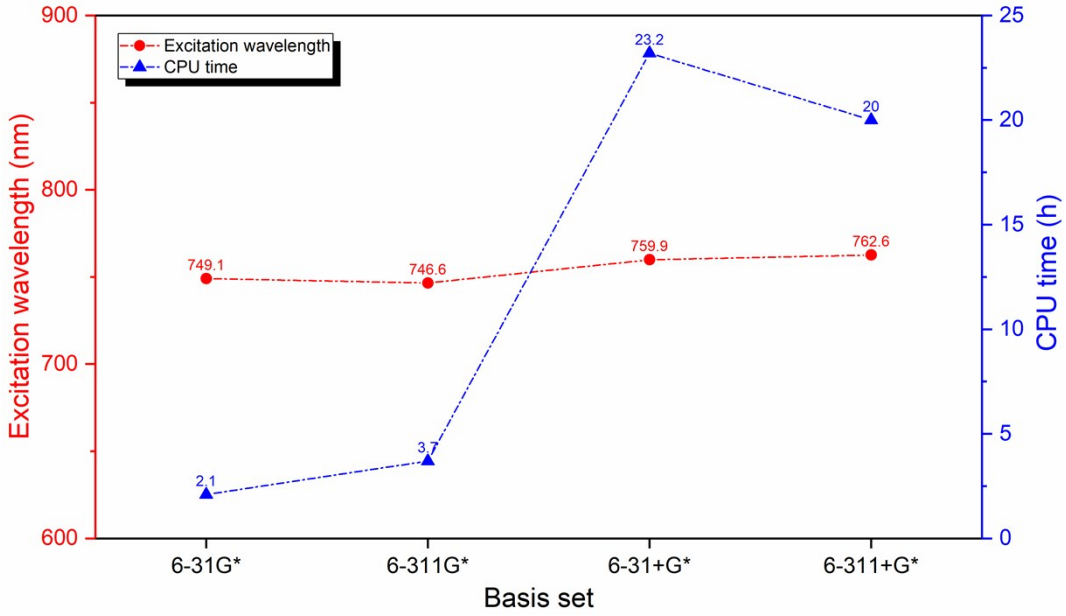

Figure S2. The effect of basis sets extending from 6-31G*, 6-311G*, 6-31+G* and 6-311+G* on the absorption wavelengths λ_{01} of D-BBT-D molecule using the ωB97X* functional.

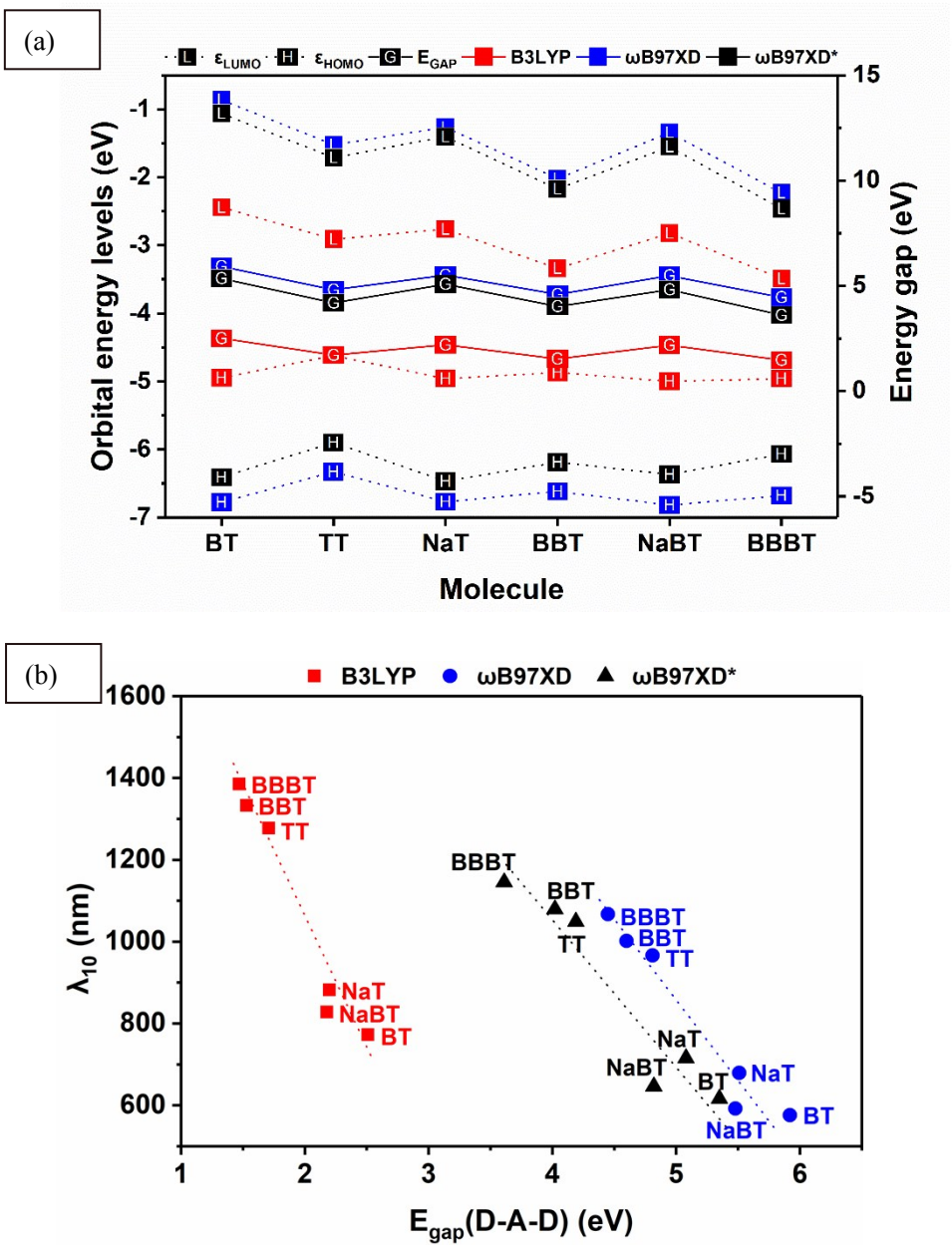

Figure S3. (a) Calculated orbital energies and energy gaps of six selected molecules using B3LYP, ωB97XD and ωB97XD* functionals; (b) calculated fluorescence emission wavelength (λ_{10}) of various D-A-D fluorophores as a function of their corresponding HOMO-LUMO energy gap using B3LYP, ωB97XD and ωB97XD* functionals.

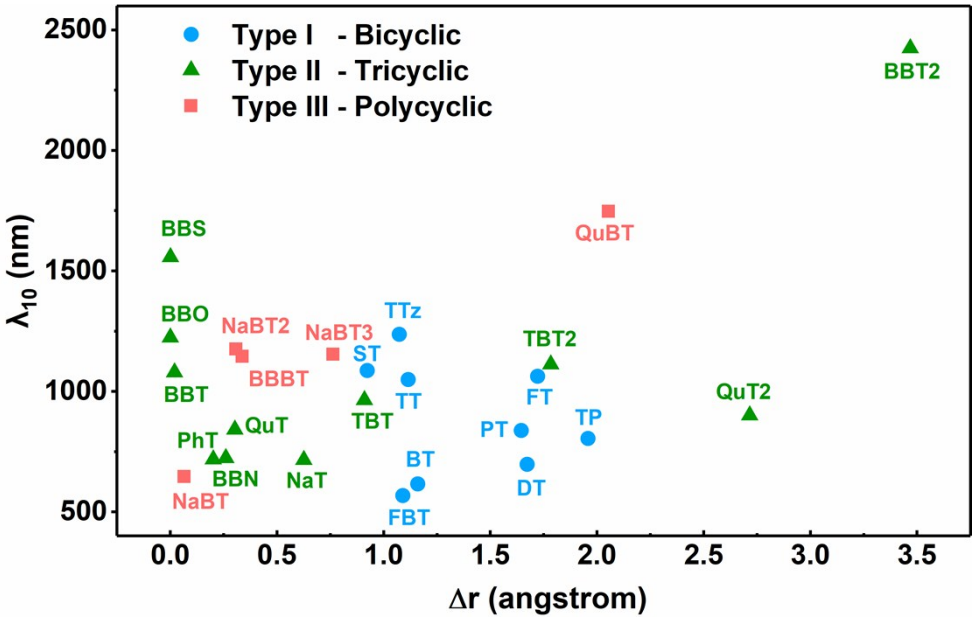

Figure S4. Calculated fluorescence wavelengths λ_{10} (nm) of various D-A-D fluorophores as a function of corresponding hole-electron distance Δr (Å) at the ωB97X*/6-31G(d) level.

Table S1. Optimal range-separation parameters ($bohr^{-1}$), HOMO and LUMO energy levels (eV), energy gaps (eV), dihedral angles (°) of ground S_0 and excited S_1 states, fluorescence wavelength (nm), emission energies (eV), oscillator strength f_{10}, and hole-electron distance (Δr) for various pure acceptor and D-A-D fluorophores.

	Molecule	ω	ε_{LUMO}(A)/eV	ε_{HOMO}(A)/eV	E_{GAP}(A)/eV	ε_{LUMO}(DAD)/eV	ε_{HOMO}(DAD)/eV	E_{GAP}(DAD)/eV	dihedral(S_0)/°	dihedral(S_1)/°	E_{10}/eV	λ_{10}/nm	f_{10}	distance/Å
Bicyclic	FBT	0.154	-0.71	-9.16	8.45	-1.11	-6.56	5.45	37.4	28.9	2.18	568	0.9978	1.09
	BT	0.146	-0.58	-8.89	8.31	-1.06	-6.41	5.35	36.8	18.9	2.01	616	0.9828	1.16
	DT	0.144	-1.27	-9.73	8.46	-1.69	-6.46	4.77	9.5	0.8	1.78	697	1.1150	1.67
	TP	0.132	-0.50	-8.47	7.97	-1.22	-6.07	4.85	20.3	1.6	1.54	805	0.7428	1.96
	PT	0.132	-0.30	-7.70	7.40	-1.10	-5.76	4.66	2.7	2.1	1.48	838	0.4420	1.64
	TT	0.132	-1.05	-8.19	7.13	-1.71	-5.90	4.19	3.1	1.2	1.18	1049	0.6006	1.11
	FT	0.134	-0.93	-8.15	7.22	-1.60	-5.83	4.23	0.4	1.1	1.17	1063	0.4481	1.72
	ST	0.129	-1.10	-8.04	6.93	-1.75	-5.84	4.09	4.4	1.2	1.14	1087	0.6071	0.92
	TTz	0.135	-1.25	-9.40	8.15	-1.88	-6.28	4.40	18.2	4.6	1.00	1237	0.4095	1.07
Tricyclic	NaT	0.154	-1.19	-7.63	6.44	-1.40	-6.47	5.08	53.6	44.0	1.73	715	0.5662	0.63
	BBN	0.131	-0.64	-7.94	7.30	-1.28	-6.05	4.77	28.5	13.7	1.73	718	1.4483	0.20
	PhT	0.140	-1.56	-8.56	7.00	-1.82	-6.49	4.66	48.6	42.3	1.72	723	0.7700	0.98
	QuT	0.139	-1.55	-8.39	6.84	-1.81	-6.33	4.52	44.0	38.0	1.47	842	0.6719	0.30
	QuT2	0.153	-1.92	-8.74	6.82	-2.11	-6.51	4.40	43.9	30.7	1.38	900	0.2717	2.72
	TBT	0.132	-1.45	-7.05	5.59	-1.73	-6.04	4.31	47.0	42.3	1.29	964	0.4268	0.91
	BBT	0.134	-1.95	-8.13	6.18	-2.17	-6.19	4.02	36.2	30.2	1.15	1079	0.6397	0.02
	TBT2	0.132	-1.45	-7.05	5.59	-1.77	-5.90	4.14	39.9	29.3	1.11	1112	0.2967	1.78
	BBO	0.154	-2.41	-8.55	6.13	-2.66	-6.01	3.35	18.2	8.8	1.01	1224	0.4819	0.00
	BBS	0.126	-2.17	-7.72	5.55	-2.26	-6.26	4.00	38.6	32.6	0.80	1557	0.7981	0.00
	BBT2	0.132	-2.23	-8.09	5.86	-2.52	-5.99	3.47	19.7	5.5	0.51	2424	0.1428	3.47
Polycyclic	NaBT	0.136	-1.27	-8.28	7.01	-1.55	-6.37	4.82	34.2	23.1	1.92	646	1.2154	0.07
	BBBT	0.110	-2.33	-7.41	5.08	-2.46	-6.07	3.61	35.4	32.5	1.08	1145	1.1011	0.34
	NaBT3	0.131	-2.09	-7.15	5.06	-2.25	-6.20	3.95	52.6	44.7	1.07	1154	0.3466	0.76
	NaBT2	0.130	-2.09	-7.15	5.06	-2.25	-6.18	3.93	52.3	46.0	1.06	1175	0.3368	0.31

QuBT	0.130	-2.72	-8.03	5.31	-2.83	-6.19	3.36	42.2	38.5	0.71	1747	0.3073	2.05

Table S2. The calculated absorbance excitation energies E_{01} (in eV)/wavelengths λ_{01} (in nm) and fluorescence emission energies E_{10} (in eV)/wavelengths λ_{10} (in nm) using various DFT methods in comparison with the available experimental data for D-BBT-D molecule.

DFT Methods	λ_{01}	$\Delta\lambda_{01}$	E_{01}	ΔE_{01}	λ_{10}	$\Delta\lambda_{10}$	E_{10}	ΔE_{10}
PBE	1371	621	0.90	-0.75	1816	761	0.68	-0.50
B3LYP	1005	255	1.23	-0.42	1333	278	0.93	-0.25
M062X	705	-45	1.76	0.11	1028	-27	1.22	0.04
ωB97XD	678	-72	1.83	0.18	1002	-53	1.25	0.07
ωB97XD*	749	-1	1.66	0.01	1079	24	1.15	-0.03
Exp[a]	750		1.65		1055		1.18	

[a]The measured experimental data for absorption and emission wavelengths were taken from the work of Dai et al. [*Nature materials 2016, 15(2), 235*]

Table S3. HOMO and LUMO energy levels (eV), energy gaps (eV), fluorescence wavelength (nm), emission energies (eV) and oscillator strength f_{10} for various typical D-A-D fluorophores at the PCM(water)-TD-DFT/6-31G(d) level.

	PCM(water)-TD-B3LYP/6-31G(d)						
	Molecule	ε_{LUMO}/eV	ε_{HOMO}/eV	E_{GAP}/eV	E_{10}/eV	λ_{10}/nm	f_{10}
Bicyclic	BT	-2.44	-4.95	2.51	1.61	772	0.6881
	TT	-2.91	-4.62	1.71	0.97	1277	0.5162
Tricyclic	NaT	-2.76	-4.96	2.20	1.41	882	0.4712
	BBT	-3.34	-4.87	1.53	0.93	1333	0.5967
Polycyclic	NaBT	-2.82	-5.00	2.18	1.50	828	0.8360
	BBBT	-3.49	-4.96	1.47	0.90	1385	1.0336

	PCM(water)-TD-ωB97XD/6-31G(d)						
	Molecule	ε_{LUMO}/eV	ε_{HOMO}/eV	E_{GAP}/eV	E_{10}/eV	λ_{10}/nm	f_{10}
Bicyclic	BT	-0.86	-6.78	5.92	2.15	576	1.1078
	TT	-1.52	-6.33	4.81	1.28	966	0.6615
Tricyclic	NaT	-1.26	-6.77	5.51	1.83	679	0.6000
	BBT	-2.02	-6.62	4.60	1.24	1002	0.6946
Polycyclic	NaBT	-1.34	-6.82	5.48	2.09	592	1.3835
	BBBT	-2.23	-6.68	4.45	1.16	1067	1.1985

	PCM(water)-TD-ωB97XD*/6-31G(d)						
	Molecule	ε_{LUMO}/eV	ε_{HOMO}/eV	E_{GAP}/eV	E_{10}/eV	λ_{10}/nm	f_{10}
Bicyclic	BT	-1.06	-6.41	5.35	2.01	616	0.9828
	TT	-1.71	-5.90	4.19	1.18	1049	0.6006
Tricyclic	NaT	-1.40	-6.47	5.08	1.73	715	0.5662
	BBT	-2.17	-6.19	4.02	1.15	1079	0.6397
Polycyclic	NaBT	-1.55	-6.37	4.82	1.92	646	1.2154
	BBBT	-2.46	-6.07	3.61	1.08	1145	1.1011