Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Aza-Boron-Dipyrromethene Dyes: TD-DFT Benchmarks, Spectral Analysis and Design of Original Near-IR Structures

Electronic Supplementary Information

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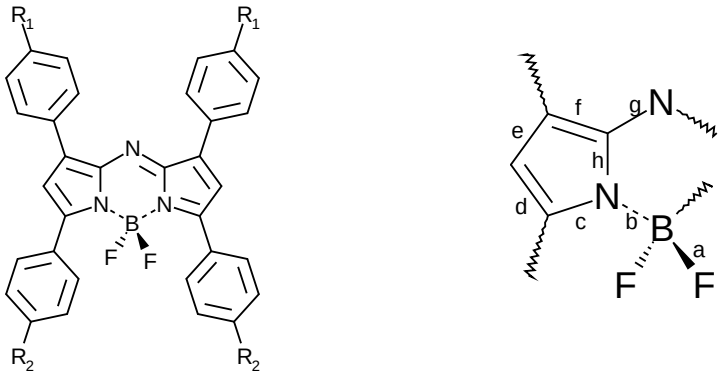

Scheme ESI-1: Representation of the aza-BODIPY dyes investigated herein.

Table ESI-1: Impact of the atomic basis set on the computed transition wavelengths (in nm) and oscillator strengths (between brackets). The structure, **1**, corresponds to R_1=R_2=H in Scheme ESI-1 has been used. All calculations have been performed at the PCM($CHCl_3$)-TD-PBE0/**X**//PCM($CHCl_3$)-PBE0/6-311G(d,p) level of approximation. Only the major bands ($f > 0.1$) are reported.

Basis (**X**)	λ_1 (f_1)	λ_2 (f_2)	λ_3 (f_3)
6-31G	564 (0.90)	449 (0.41)	355 (0.19)
6-31G(d)	583 (0.87)	453 (0.37)	357 (0.19)
6-31G(d,p)	583 (0.87)	453 (0.37)	357 (0.19)
6-31+G(d)	593 (0.87)	455 (0.39)	358 (0.19)
6-31++G(d,p)	593 (0.87)	455 (0.39)	358 (0.19)
6-31+G(2d)	598 (0.86)	455 (0.38)	358 (0.19)
6-31+G(2d,p)	598 (0.86)	455 (0.38)	358 (0.19)
6-31++G(2d,2p)	598 (0.86)	455 (0.38)	358 (0.19)
6-311G(d)	591 (0.87)	454 (0.38)	358 (0.19)
6-311G(d,p)	591 (0.87)	454 (0.38)	357 (0.19)
6-311+G(d)	596 (0.87)	456 (0.39)	358 (0.19)
6-311++G(d,p)	597 (0.87)	455 (0.39)	358 (0.19)
6-311+G(2d,p)	599 (0.86)	455 (0.38)	358 (0.19)
6-311++G(2d,2p)	599 (0.86)	455 (0.38)	358 (0.19)
6-311++G(2df,2pd)	600 (0.86)	455 (0.38)	358 (0.19)

Table ESI-2: Impact of the selected basis set on the bond lengths (in Å) for the compound of Table ESI-1. All calculations at the PCM($CHCl_3$)-PBE0/**X**.

Basis (**X**)	a	b	c	d	e	f	g	h
6-31G	1.437	1.547	1.372	1.417	1.391	1.435	1.323	1.404
6-31G(d)	1.388	1.565	1.358	1.414	1.384	1.435	1.316	1.389
6-31G(d,p)	1.389	1.565	1.358	1.414	1.384	1.435	1.316	1.389
6-31G(2d,2p)	1.381	1.561	1.356	1.413	1.383	1.433	1.315	1.387
6-311G(d)	1.393	1.561	1.356	1.412	1.382	1.433	1.316	1.388
6-311G(d,p)	1.393	1.561	1.356	1.412	1.382	1.433	1.316	1.388
6-311G(2d,p)	1.385	1.560	1.354	1.410	1.380	1.431	1.312	1.387
6-311G(2d,2p)	1.386	1.560	1.354	1.410	1.380	1.431	1.312	1.387
6-311++G(d,p)	1.397	1.559	1.357	1.412	1.383	1.433	1.314	1.389
6-311++G(2d,2p)	1.388	1.559	1.355	1.410	1.380	1.431	1.312	1.388
cc-pVTZ	1.387	1.563	1.354	1.410	1.379	1.431	1.312	1.387

Table ESI-3: Impact of the selected basis set on the valence angles (in degrees), see caption of Table ESI-2.

Basis (**X**)	α_{FBF}	α_{BNC}	α_{NCN}
6-31G	109.1	122.0	123.4
6-31G(d)	111.5	122.3	124.2
6-31G(d,p)	111.5	122.3	124.2
6-31G(2d,2p)	111.3	122.3	124.3
6-311G(d)	111.0	122.1	124.3
6-311G(d,p)	111.0	122.1	124.3
6-311G(2d,p)	111.1	122.1	124.3
6-311G(2d,2p)	111.1	122.1	124.3
6-311++G(d,p)	110.6	122.1	124.3
6-311++G(2d,2p)	110.9	122.1	124.2
cc-pVTZ	111.0	122.1	124.1

Table ESI-4: Variations of the PCM($CHCl_3$)-TD-PBE0/6-311+G(2d,p) transition wavelengths as a function of the basis set used to optimize the geometry.

Basis (**X**)	λ_1 (f_1)	λ_2 (f_2)	λ_3 (f_3)
6-31G	622 (0.85)	471 (0.39)	367 (0.20)
6-31G(d)	604 (0.86)	458 (0.38)	358 (0.20)
6-31G(d,p)	604 (0.86)	458 (0.38)	359 (0.19)
6-31G(2d,2p)	602 (0.86)	456 (0.37)	358 (0.20)
6-311G(d)	598 (0.87)	455 (0.38)	358 (0.19)
6-311G(d,p)	599 (0.86)	455 (0.38)	358 (0.19)
6-311G(2d,p)	596 (0.87)	453 (0.37)	356 (0.19)
6-311G(2d,2p)	597 (0.87)	453 (0.37)	356 (0.19)
6-311++G(d,p)	595 (0.86)	455 (0.38)	359 (0.19)
6-311++G(2d,2p)	594 (0.87)	453 (0.37)	357 (0.19)
cc-pVTZ	594 (0.87)	453 (0.37)	356 (0.19)

Table ESI-5: Structural parameters (bond lengths in Å, valence angles in degrees), obtained for the R_1=H, R_2=Br derivative (see Scheme ESI-1 or **2** in Scheme 1). The experimental values are taken from literature.[1] All values are computed with the 6-311G(2d,p) basis set without solvent effect.

	Bond lengths								Valence angles		
Functional	a	b	c	d	e	f	g	h	α_{FBF}	α_{BNC}	α_{NCN}
Experiment (1)	1.392	1.557	1.368	1.418	1.362	1.438	1.327	1.398	110.1	121.6	124.5
Experiment (2)	1.377	1.564	1.365	1.398	1.390	1.433	1.322	1.401		121.3	124.0
Experiment (average)	1.384	1.561	1.366	1.408	1.376	1.435	1.325	1.399	110.1	121.4	124.2
PBE	1.398	1.573	1.371	1.421	1.390	1.444	1.325	1.397	111.6	122.1	124.4
TPSS	1.396	1.572	1.372	1.418	1.389	1.441	1.325	1.397	111.4	122.2	124.3
TPSSh	1.390	1.568	1.364	1.415	1.384	1.436	1.320	1.392	111.4	122.2	124.3
O3LYP	1.385	1.575	1.357	1.414	1.383	1.437	1.317	1.390	112.1	122.2	124.3
B3LYP	1.388	1.569	1.360	1.414	1.383	1.436	1.317	1.394	111.4	122.1	124.2
PBE0	1.382	1.563	1.353	1.411	1.379	1.431	1.323	1.385	111.6	122.2	124.3
BMK	1.378	1.559	1.348	1.420	1.383	1.437	1.312	1.388	111.5	122.3	124.1
M05-2X	1.383	1.567	1.346	1.413	1.378	1.428	1.310	1.390	111.6	122.5	124.4
LC-PBE	1.373	1.547	1.327	1.401	1.363	1.413	1.299	1.379	111.5	122.5	124.0
LC-ωPBE	1.383	1.564	1.335	1.410	1.371	1.423	1.308	1.335	111.9	122.6	124.1
CAM-B3LYP	1.381	1.563	1.346	1.410	1.376	1.427	1.310	1.391	111.4	122.3	124.0
ωB97	1.394	1.573	1.343	1.417	1.379	1.429	1.314	1.396	111.6	122.4	124.3
ωB97X	1.387	1.569	1.342	1.414	1.377	1.427	1.311	1.393	111.7	122.4	124.2
ωB97XD	1.383	1.567	1.344	1.412	1.378	1.426	1.309	1.389	111.6	122.5	124.3

Table ESI-6: Structural parameters (bond lengths in Å, valence angles in degrees), obtained for the R_1=H, R_2=OMe derivative (see Scheme ESI-1 or **3** in Scheme 1). The experimental values are taken from literature.[2] All values are computed with the 6-311G(2d,p) basis set without solvent effect.

	Bond lengths								Valence angles		
Functional	a	b	c	d	e	f	g	h	α_{FBF}	α_{BNC}	α_{NCN}
Experiment (1)	1.365	1.563	1.360	1.399	1.376	1.436	1.317	1.409	110.1	121.5	124.9
Experiment (2)	1.376	1.562	1.360	1.408	1.374	1.426	1.326	1.396		122.6	124.2
Experiment (average)	1.371	1.562	1.360	1.404	1.375	1.431	1.321	1.402	110.1	122.0	124.6
PBE	1.400	1.572	1.374	1.422	1.390	1.443	1.325	1.397	111.3	121.9	124.4
TPSS	1.399	1.571	1.375	1.420	1.388	1.440	1.326	1.398	111.0	122.0	124.4
TPSSh	1.392	1.567	1.367	1.416	1.383	1.435	1.320	1.393	111.1	122.1	124.4
O3LYP	1.387	1.574	1.360	1.416	1.382	1.436	1.328	1.390	111.8	121.9	124.4
B3LYP	1.390	1.568	1.362	1.416	1.382	1.435	1.317	1.394	111.1	121.9	124.2
PBE0	1.384	1.562	1.355	1.413	1.378	1.430	1.313	1.386	111.3	122.0	124.4
BMK	1.380	1.557	1.350	1.421	1.382	1.436	1.313	1.389	111.2	122.2	124.1
M05-2X	1.385	1.566	1.348	1.416	1.376	1.428	1.311	1.390	111. 4	122.3	124.6
LC-PBE	1.375	1.547	1.329	1.404	1.362	1.413	1.299	1.379	111.2	122.3	124.1
LC-ωPBE	1.385	1.564	1.338	1.412	1.370	1.423	1.307	1.390	111.7	122.3	124.2
CAM-B3LYP	1.384	1.562	1.348	1.413	1.375	1.427	1.310	1.391	111.2	122.1	124.1
ωB97	1.396	1.572	1.346	1.420	1.377	1.429	1.314	1.396	111.4	122.1	124.4
ωB97X	1.389	1.568	1.345	1.417	1.375	1.426	1.311	1.393	111.4	122.0	124.3
ωB97XD	1.386	1.566	1.348	1.415	1.376	1.425	1.309	1.390	111.5	122.0	124.4

Table ESI-7: List of major computed bands for **4** with a PCM(CH_2Cl_2)-TD-X/6-311+G(2d,p)//PCM(CH_2Cl_2)-PBE0/6-311G(2d,p) scheme. All values in nm. Experimental values are from.[3]

Functional	λ_1 (f_1)	λ_2 (f_2)	λ_3 (f_3)	λ_4 (f_4)
PBE	1267 (0.54)	1083 (0.56)	659 (0.60)	
TPSS	1212 (0.55)	1042 (0.57)	645 (0.61)	
TPSSh	1021 (0.62)	888 (0.60)	610 (0.55) & 497 (0.44)	423 (1.30)
O3LYP	1011 (0.62)	880 (0.58)	612 (0.54) & 499 (0.43)	424 (1.36)
B3LYP	885 (0.76)	764 (0.64)	584 (0.42) & 471 (0.46)	395 (1.84)
PBE0	834 (0.85)	712 (0.68)	565 (0.35) & 454 (0.47)	379 (2.04)
M06	810 (0.91)	622 (0.68)	457 (0.47)	381 (1.93)
BMK	711 (1.14)	562 (0.89)	411 (0.43)	343 (2.32)
M05-2X	688 (1.22)	493 (1.17)	394 (0.34)	329 (2.24)
LC-PBE	672 (1.19)			361 (2.62)
LC-ωPBE	669 (1.18)			369 (2.41)
CAM-B3LYP	679 (1.21)	467 (1.31)	394 (0.23)	328 (2.09)
ωB97	673 (1.18)			369 (2.46)
ωB97X	665 (1.19)			382 (2.31)
ωB97XD	662 (1.21)			417 (1.97)
Exp	745 (m)	623 (w)	482 (vw)	359 (s)

Table ESI-8: List of major computed bands for **5** with a PCM(CH_2Cl_2)-TD-X/6-311+G(2d,p)//PCM(CH_2Cl_2)-PBE0/6-311G(2d,p) scheme. All values in nm. Experimental values are from.[1]

Functional	λ_1 (f_1)	λ_2 (f_2)	λ_3 (f_3)
PBE	852.4 (0.92)	706 (1.03)	
TPSS	829 (0.95)	687 (1.07)	
TPSSh	750 (1.09)	619 (0.63)	571 (0.74)
O3LYP	751 (1.09)	617 (0.64)	572 (0.73)
B3LYP	713 (1.18)	559 (0.97)	505(0.82)
PBE0	690 (1.22)	526 (1.14)	460 (0.83)
M06	701 (1.20)	521 (1.28)	463 (0.89)
BMK	647 (1.27)	448 (1.61)	379 (1.54)
M05-2X	649 (1.24)	417 (2.09)	349 (1.57)
LC-PBE	655 (1.17)	353 (1.90)	326 (2.25)
LC-ωPBE	652 (1.16)	362 (1.60)	333 (2.45)
CAM-B3LYP	648(1.22)	414 (1.99) & 382 (0.72)	349 (1.15)
ωB97	657 (1.16)	362 (1.75)	333 (2.32)
ωB97X	647 (1.18)	374 (1.64)	343 (2.33)
ωB97XD	641 (1.20)	400 (1.51)	364 (2.03)
Exp	694 (s)	492 (m)	373 (s)

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(3) Bouit, P. A.; Kamada, K.; Feneyrou, P.; Berginc, G.; Toupet, L.; Maury, O.; Andraud, C. *Adv. Mater.* **2009**, *21*, 1151–1154.