Supporting Information

Unusual Spectroscopic and Photophysical Properties of *meso-tert*-ButylBODIPY in Comparison to Related Alkylated BODIPY Dyes

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Experimental Section

Instrumentation

The NMR experiments were performed on Bruker Avance 300 (for 1-4) and Bruker Avance 500 (for 5) NMR spectrometers at room temperature. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS). Chemical shift multiplicities are reported as s = singlet and d = doublet. Melting points were determined with an X-4 melting-point apparatus (manufactured by Henan, Gongyi Factory, China) and are uncorrected. High-resolution mass spectra were obtained using APCI-TOF in positive mode. Absorption spectra were recorded with a Perkin-Elmer Lambda 650 UV/Vis spectrophotometer with a Peltier temperature-controlled cell holder. All measurements were made at 20 °C, using 5×10 mm cuvettes. Steady-state spectra were collected a JASCO fluorescence emission on FP-6500 spectrofluorometer equipped with a 450 W xenon lamp for excitation, with temperature controller ETC-273T at 20 °C, using 5×10 mm cuvettes.

Relative Determination of Fluorescence Quantum Yield Φ

For the relative determination of the fluorescence quantum yield Φ in a series of solvents, the following formula (eq S1) was used:^{1,2}

$$\Phi_{x} = \Phi_{r} \times \frac{F_{x}}{F_{r}} \times \frac{1 - 10^{-A_{r}(\lambda_{ex})}}{1 - 10^{-A_{x}(\lambda_{ex})}} \times \frac{n_{x}^{2}}{n_{r}^{2}}$$
(S1)

The subscripts x and r refer respectively to sample x (i.e., BODIPY derivatives 1-5) and reference (standard) fluorophore r with known quantum yield Φ_r in a specific solvent; F stands for the *spectrally corrected*, integrated fluorescence spectra; $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength λ_{ex} ; *n* represents the refractive index of the solvent (in principle at the average emission wavelength). To minimize inner filter effects, the absorbance at the excitation wavelength λ_{ex} was kept under 0.1. The measurements were performed using 5×10 mm cuvettes, with 10 mm optical path length for absorption and a right-angle (L-) arrangement for fluorescence emission collection, using excitation through the long side and emission collection through the shorter side, to avoid auto-absorption inner-filter effect. Fluorescein in 0.1 N NaOH was used as fluorescence quantum yield reference ($\Phi_r = 0.90$).³ All measurements were done on non-degassed samples at 20 °C. The averages and standard uncertainties of Φ reported in Tables 3 and S2–S5 are computed from eight independent Φ measurements, resulting from (2 conc. of sample x) × (2 conc. of reference r) × (2 excitation wavelengths λ_{ex} = 460 and 470 nm). Note that 460 and 470 nm were selected as λ_{ex} because they allow one to collect the complete emission spectrum, required for the integration of the spectral band.

Time-resolved Fluorescence

Fluorescence decay traces were recorded by the single photon timing method,^{4,5,6,7}

using the FluoTime200 fluorometer (PicoQuant GmbH). The excitation source consisted of a 485 nm pulsed diode laser (LDH series from PicoQuant GmbH) with a minimum pulse width of 88 ps, and operated at a pulse repetition rate of 10 or 20 MHz, depending on the compound probed. Fluorescence decay histograms were collected at three different emission wavelengths selected by a grating monochromator, after a polarizer set at the 'magic angle' to avoid polarization artifacts. The fluorescence decay traces were collected over 1320 channels, with a time increment of 36 ps per channel, until they reached 2×10^4 counts in the peak channel. Histograms of the instrument response functions were collected using a LUDOX scatterer.

Crystal Structure Determination

Crystals of BODIPYs 1, 2, 4 and 5 suitable for X-ray structural analysis were obtained by slow diffusion of hexane into their dichloromethane solutions at room temperature over a one-week period. The vial containing this solution was loosely capped to promote the crystallization upon hexane diffusion. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART⁸ software and refined using SAINT⁹ on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo K α radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software, which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2 , SHELXL-97,¹⁰ incorporated in SHELXTL V5.10.¹¹ The crystallographic data of 1, 2, 4 and 5 are compiled in Table S1. CCDC 995007 (1), CCDC 995010 (2), CCDC 995008 (4) and CCDC 995009 (5) contain the supplementary crystallographic data for this paper and be obtained free of charge via can www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Crystallographic Data for 1, 2, 4 and 5

	1	2	4	5
Formula	$C_{10}H_9BF_2N_2$	$C_{13}H_{15}BF_2N_2$	$C_{17}H_{23}BF_2N_2$	$C_{24}H_{26}B_2F_4N_4$
M (g/mol)	206.00	248.08	304.18	468.11
Crystal system	triclinic	orthorhombic	triclinic	monoclinic
Space group	P-1	Pna2(1)	P-1	C2/c
<i>a</i> (Å)	7.7265(7)	14.254(2)	10.9260(9)	16.054(2)
<i>b</i> (Å)	7.7446(7)	13.5629(19)	12.1904(10)	12.6204(19)
<i>c</i> (Å)	16.6941(15)	6.4554(9)	13.1824(11)	13.685(3)
α (°)	102.946(1)	90.00	103.996(1)	90.00
$eta(^\circ)$	93.552(1)	90.00	99.116(1)	120.228(1)
γ (°)	92.329(1)	90.00	90.038(1)	90.00
$V(Å^3)$	970.16(15)	1248.0(3)	1680.8(2)	2395.7(8)
Ζ	4	4	4	4
$T(\mathbf{K})$	293	293	293	293
$\rho_{calcd} \left(g \ cm^{-3}\right)$	1.410	1.320	1.202	1.298
μ (Mo K α) (mm ⁻¹)	0.111	0.099	0.085	0.098
<i>F</i> (000)	424.0	520.0	648.0	976.0
Crystal size (mm ³)	0.15×0.13×0.12	0.16×0.14×0.12	0.15×0.13×0.12	0.13×0.12×0.1
Reflections measured	8480	10436	14676	9286
Unique reflections	4380	2786	7576	4704
R(int)	0.0194	0.0509	0.0208	0.0260
wR_2 (all data)	0.1379	0.2688	0.1293	0.0987
R_1 (>2sigma(I))	0.0454	0.0764	0.0462	0.0373
CCDC deposition no	995007	995010	995008	995009

Table S1. Crystallographic data for 1, 2, 4 and 5, measured in this work at Anhui Normal University (China).

Synthesis

The synthesis of 1–5, completed at Anhui Normal University (China), is described in the main paper.



Scheme S1. The attempted synthesis of *meso-tert*-butylBODIPY 6 resulted in *meso-*unsubstituted BODIPY 7.

Initially, we rationalized that the unusually low Φ -values for **2** may be due to the free rotation of the *tert*-butyl group, which promotes the nonradiative decay (internal conversion) process. Therefore, if we could restrict the free rotation of the *tert*-butyl group by installing methyl groups at the 1,7-positions of BODIPY (as in compound **6**, 8-*tert*-butyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene, Scheme S1), we might be able to improve the fluorescence quantum yield. However, the condensation of pivaloyl chloride with 2,4-dimethylpyrrole in dichloromethane gave only the *meso*-unsubstituted compound **7** after the subsequent BF₂ complexation reaction.

Synthesis of 7 [4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene]: Pivaloyl chloride (368 µL, 3 mmol) was added dropwise to freshly distilled 2,4dimethylpyrrole (665 mg, 7 mmol) in 100 mL dry dichloromethane. The reaction mixture was stirred at room temperature for 12 h under argon. Then triethylamine (3 mL) and BF₃·Et₂O (8 mL) were added to the reaction mixture at ice-cold condition. The reaction mixture was stirred at room temperature for 2 h, washed with water, dried over anhydrous Na₂SO₄, and filtered. The solvent was then evaporated under vacuum and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to give 7 in 6% yield (45 mg). ¹H NMR (300 MHz, CDCl₃): δ 7.04 (s, 1 H), 6.04 (s, 2 H), 2.53 (s, 6 H), 2.25 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃): δ 156.7, 141.2, 133.4, 120.1, 119.0, 14.6, 11.2. The data correspond to those of the literature.¹²



Photographs of Cuvettes with 1 and 2 in Chloroform and Acetone

Chart S1. Photographs of cuvettes containing 1 and 2 in acetone and chloroform under ambient light (top) and 365 nm irradiation (bottom).

Spectroscopic and Photophysical Data

All spectroscopic and photophysical data of 1–5 were measured at the University of Granada (Spain).



Figure S1. (a) Normalized, main $S_1 \leftarrow S_0$ visible absorption bands of **3** in the solvents indicated. (b) Corresponding normalized fluorescence emission spectra upon excitation at 470 nm.



Figure S2. (a) Normalized, main $S_1 \leftarrow S_0$ visible absorption bands of **4** in the solvents indicated. (b) Corresponding normalized fluorescence emission spectra upon excitation at 470 nm.



Figure S3. (a) Normalized, main $S_1 \leftarrow S_0$ visible absorption bands of **5** in the solvents indicated. (b) Corresponding normalized fluorescence emission spectra upon excitation at 470 nm.



Figure S4. Fluorescence decay traces and corresponding weighted residuals from mono-exponential fits of **2** in dichloromethane (black), methanol (red) and chlorobenzene (blue). $\lambda_{ex} = 485$ nm, $\lambda_{em} = 565$ nm.



Figure S5. Fluorescence decay traces and corresponding weighted residuals from mono-exponential fits of **4** in dibutyl ether (black), methanol (red) and chlorobenzene (blue). $\lambda_{ex} = 485$ nm, $\lambda_{em} = 510$ nm.



Figure S6. Fluorescence decay traces and corresponding weighted residuals from mono-exponential fits of **5** in dibutyl ether (black), methanol (red) and chlorobenzene (blue). $\lambda_{ex} = 485 \text{ nm}, \lambda_{em} = 510 \text{ nm}.$

	Solvent	$\lambda_{abs}(max)$	$\lambda_{em}(max)$	$\Delta \overline{\nu}$	fwhm _{abs}	fwhm _{em}	Φ^{b}	τ ^c	$k_{\mathrm{f}}{}^d$
	Bolvent	/ nm	/ nm	$/ cm^{-1}$	/ cm ⁻¹	/ cm ⁻¹	Ψ	/ ns	$/ 10^8 \ s^{-1}$
1	CH ₃ OH	491	500	367	1037	1031	1.00 ± 0.03	6.91	1.45 ± 0.05
2	CH ₃ CN	489	499	410	1066	1065	1.00 ± 0.06	6.73	1.49 ± 0.09
3	$(C_2H_5)_2O$	493	501	324	877	985	1.00 ± 0.04	6.73	1.49 ± 0.05
4	(CH ₃) ₂ CO	490	500	408	1017	1059	1.00 ± 0.04	6.88	1.45 ± 0.06
5	t-BuOMe ^e	493	501	324	877	993	1.00 ± 0.04	6.65	1.50 ± 0.05
6	EtOAc ^e	491	500	367	1013	1019	1.00 ± 0.03	6.47	1.55 ± 0.05
7	Hexane	496	501	201	676	899	1.00 ± 0.05	6.46	1.55 ± 0.07
8	Bu ₂ O ^e	496	503	281	784	943	1.00 ± 0.05	6.21	1.61 ± 0.07
9	THF ^e	493	502	364	960	1018	1.00 ± 0.03	6.13	1.63 ± 0.06
10	$\mathrm{CH}_2\mathrm{Cl}_2$	495	503	321	870	970	1.00 ± 0.04	6.23	1.61 ± 0.06
11	CHCl ₃	497	504	279	820	933	1.00 ± 0.02	6.30	1.59 ± 0.03
12	Toluene	498	507	356	856	1009	1.00 ± 0.04	5.63	1.78 ± 0.08
13	PhCl ^e	499	507	316	856	997	1.00 ± 0.04	5.66	1.77 ± 0.07

Table S2. Spectroscopic and photophysical data of 1 as a function of solvent.^a

^{*b*} Fluorescence quantum yield \pm one standard uncertainty. Φ determined vs. fluorescein in 0.1 N NaOH ($\Phi_r = 0.90$) as reference.

^{*c*} Globally determined fluorescence lifetime. The standard errors on τ , obtained from the diagonal elements of the covariance matrix available from the global analysis fit of decay traces recorded at three different emission wavelengths ($\lambda_{em} = 510$, 515 and 520 nm. $\lambda_{ex} = 485$ nm), are between 19 and 23 ps.

^{*d*} Fluorescence rate constant $(k_f) \pm$ propagated error. Because Φ is 1.00 in all solvents studied, the rate constant for nonradiative decay (k_{nr}) is vanishingly small. The propagated errors are calculated using the standard uncertainties on Φ and the standard errors on τ . The propagated errors on k_{nr} are between 3 × 10⁶ s⁻¹ and 9 × 10⁶ s⁻¹.

^{*e*} *t*-BuOMe = *tert*-butyl methyl ether (MTBE), EtOAc = ethyl acetate, Bu_2O = dibutyl ether, THF = tetrahydrofuran, PhCl = chlorobenzene.

	Salvant	$\lambda_{abs}(max)$	$\lambda_{em}(max)$	$\Delta \overline{\nu}$	fwhm _{abs}	fwhm _{em}	Φh	τ ^c	$k_{\mathrm{f}}{}^{d}$	$k_{ m nr}{}^d$
	Solvent	/ nm	/ nm	$/ cm^{-1}$	/ cm ⁻¹	/ cm ⁻¹	Ψ^{v}	/ ns	$/ 10^8 \ s^{-1}$	$/ 10^8 \ s^{-1}$
1	CH ₃ OH	500	510	392	1062	1064	1.00 ± 0.04	6.53	1.53 ± 0.06	0.00 ± 0.06
2	CH ₃ CN	500	510	392	1129	1066	1.00 ± 0.05	6.65	1.50 ± 0.08	0.00 ± 0.08
3	$(C_2H_5)_2O$	502	510	312	911	956	1.00 ± 0.02	6.42	1.56 ± 0.03	0.00 ± 0.03
4	(CH ₃) ₂ CO	500	510	392	862	985	1.00 ± 0.04	6.36	1.57 ± 0.06	0.00 ± 0.06
5	t-BuOMe ^e	502	511	351	856	1017	1.00 ± 0.02	6.29	1.59 ± 0.03	0.00 ± 0.03
6	EtOAc ^e	501	510	352	797	976	1.00 ± 0.05	6.12	1.63 ± 0.08	0.00 ± 0.08
7	Hexane	504	511	272	853	990	1.00 ± 0.06	6.23	1.61 ± 0.10	0.00 ± 0.10
8	Bu ₂ O ^e	504	512	310	995	999	1.00 ± 0.04	5.92	1.69 ± 0.07	0.00 ± 0.07
9	THF ^e	503	513	388	1070	1051	0.98 ± 0.03	6.02	1.63 ± 0.05	0.03 ± 0.05
10	CH_2Cl_2	505	514	347	663	891	0.98 ± 0.03	6.09	1.61 ± 0.05	0.03 ± 0.05
11	CHCl ₃	507	516	344	895	962	0.95 ± 0.02	5.82	1.63 ± 0.03	0.09 ± 0.03
12	Toluene	507	517	382	1009	1046	1.00 ± 0.04	5.38	1.86 ± 0.07	0.00 ± 0.07
13	PhCl ^e	508	518	380	848	1057	1.00 ± 0.04	5.33	1.88 ± 0.08	0.00 ± 0.08

Table S3. Spectroscopic and photophysical data of 3 as a function of solvent.^a

^{*c*} Globally determined fluorescence lifetime. The standard errors on τ , obtained from the diagonal elements of the covariance matrix available from the global analysis fit of decay traces recorded at three different emission wavelengths ($\lambda_{em} = 510$, 515 and 520 nm. $\lambda_{ex} = 485$ nm), are between 14 and 16 ps.

^{*d*} Fluorescence rate constant (k_f) or rate constant for nonradiative decay (k_{nr}) \pm propagated error. The propagated errors are calculated using the standard uncertainties on Φ and the standard errors on τ . ^{*b*, *e*} See Table S2.

	Salvant	$\lambda_{abs}(max)$	$\lambda_{em}(max)$	$\Delta \overline{\nu}$	fwhm _{abs}	fwhm _{em}	æ h	τ ^c	$k_{\mathrm{f}}{}^{d}$	$k_{ m nr}{}^d$
	Solvent	/ nm	/ nm	$/ cm^{-1}$	/ cm ⁻¹	/ cm ⁻¹	Ψ°	/ ns	$/ \ 10^8 \ s^{-1}$	$/ 10^8 \ s^{-1}$
1	CH ₃ OH	504	513	348	753	941	1.00 ± 0.03	6.77	1.48 ± 0.04	0.00 ± 0.04
2	CH ₃ CN	504	514	386	754	977	0.98 ± 0.04	5.85	1.68 ± 0.07	0.03 ± 0.07
3	$(C_2H_5)_2O$	506	514	308	653	927	1.00 ± 0.01	6.45	1.55 ± 0.02	0.00 ± 0.02
4	(CH ₃) ₂ CO	505	514	347	680	920	0.99 ± 0.03	6.89	1.44 ± 0.04	0.01 ± 0.04
5	t-BuOMe ^e	506	516	383	634	898	1.00 ± 0.04	5.63	1.78 ± 0.07	0.00 ± 0.07
6	EtOAc ^e	505	514	347	664	923	1.00 ± 0.02	5.46	1.83 ± 0.04	0.00 ± 0.04
7	Hexane	509	516	267	676	911	1.00 ± 0.04	5.76	1.74 ± 0.07	0.00 ± 0.07
8	Bu ₂ O ^e	508	518	380	731	885	0.97 ± 0.02	5.80	1.67 ± 0.03	0.05 ± 0.04
9	THF ^e	507	517	382	734	894	0.95 ± 0.02	5.63	1.69 ± 0.04	0.09 ± 0.04
10	CH_2Cl_2	509	518	341	560	847	0.95 ± 0.02	6.09	1.56 ± 0.03	0.08 ± 0.03
11	CHCl ₃	511	520	339	744	975	0.94 ± 0.01	6.10	1.54 ± 0.02	0.10 ± 0.02
12	Toluene	511	521	376	706	939	0.98 ± 0.03	5.04	1.94 ± 0.06	0.04 ± 0.06
13	PhCl ^e	512	520	300	676	926	$1.00\pm\!\!0.03$	4.88	2.05 ± 0.06	0.00 ± 0.06

Table S4. Spectroscopic and photophysical data of 4 as a function of solvent.^a

^{*c*} Globally determined fluorescence lifetime. The standard errors on τ , obtained from the diagonal elements of the covariance matrix available from the global analysis fit of decay traces recorded at three different emission wavelengths ($\lambda_{em} = 510$, 515 and 520 nm. $\lambda_{ex} = 485$ nm), are between 5 and 20 ps.

^{*d*} Fluorescence rate constant (k_f) or rate constant for nonradiative decay (k_{nr}) \pm propagated error. The propagated errors are calculated using the standard uncertainties on Φ and the standard errors on τ . ^{*b*, *e*} See Table S2.

	Solvent	$\lambda_{abs}(max)$	$\lambda_{\text{em}}(\text{max})$	$\Delta \overline{\nu}$	fwhm _{abs}	fwhm _{em}	Φ^{b}	τ ^c	$k_{\mathrm{f}}{}^{d}$
	Solvent	/ nm	/ nm	$/ \mathrm{cm}^{-1}$	/ cm ⁻¹	/ cm ⁻¹	Ψ	/ ns	$/ \ 10^8 \ s^{-1}$
1	CH ₃ OH	493	505	482	925	1219	1.00 ± 0.03	7.44	1.34 ± 0.04
2	CH ₃ CN	492	504	484	964	1204	1.00 ± 0.03	7.32	1.37 ± 0.04
3	$(C_2H_5)_2O$	495	508	517	840	1133	1.00 ± 0.04	7.39	1.35 ± 0.05
4	(CH ₃) ₂ CO	493	505	482	821	1080	1.00 ± 0.03	7.08	1.41 ± 0.04
5	t-BuOMe ^e	495	507	478	849	1182	1.00 ± 0.03	6.92	1.45 ± 0.04
6	EtOAc ^e	494	505	441	797	1172	1.00 ± 0.04	6.86	1.46 ± 0.06
7	Hexane	497	507	397	858	1203	1.00 ± 0.03	7.21	1.39 ± 0.04
8	Bu ₂ O ^e	497	507	397	905	1199	1.00 ± 0.06	6.58	1.52 ± 0.09
9	THF ^e	496	508	476	917	1186	0.99 ± 0.03	6.49	1.53 ± 0.05
10	CH_2Cl_2	497	509	474	756	1187	1.00 ± 0.04	6.59	1.52 ± 0.06
11	CHCl ₃	499	509	394	845	1234	1.00 ± 0.02	6.42	1.56 ± 0.03
12	Toluene	499	513	547	884	1187	1.00 ± 0.03	5.89	1.70 ± 0.05
13	PhCl ^e	500	512	469	833	1182	1.00 ± 0.04	5.93	1.69 ± 0.07

Table S5. Spectroscopic and photophysical data of 5 as a function of solvent.^a

^{*c*} Globally determined fluorescence lifetime. The standard errors on τ , obtained from the diagonal elements of the covariance matrix available from the global analysis fit of decay traces recorded at three different emission wavelengths ($\lambda_{em} = 510$, 515 and 520 nm. $\lambda_{ex} = 485$ nm), are between 19 and 23 ps.

^{*d*} Fluorescence rate constant $(k_f) \pm$ propagated error. Because Φ is 1.00 in all the solvents studied, except THF, the rate constant for nonradiative decay (k_{nr}) is vanishingly small. The propagated errors are calculated using the standard uncertainties on Φ and the standard errors on τ . The propagated errors on k_{nr} in all solvents, except THF, are between $3 \times 10^6 \text{ s}^{-1}$ and $9 \times 10^6 \text{ s}^{-1}$. In THF, $k_{nr} = (2 \pm 5) \times 10^6 \text{ s}^{-1}$.

^{*b*, *e*} See Table S2.

Analysis of Solvent-Dependent Spectroscopic Properties of 3–5

The analysis of the spectral maxima $\overline{\nu}_{abs}$ [= 1/ λ_{abs} (max)] and $\overline{\nu}_{em}$ [= 1/ λ_{em} (max)] as a function of the solvent was done at the KU Leuven (Belgium) using the generalized treatment of the solvent effect proposed by Catalán.¹³

The interactions of the solvent with a solute have been empirically parameterized by a large number of solvent scales. The most frequently used (and well-known) single parameters to describe the nonspecific (also called general) contribution to the solvent effect experienced by any solute are possibly $E_{\rm T}(30)$, ^{14,15,16} Kamlet, Abboud and Taft's π^* parameter,¹⁷ Dragos' S' scale,¹⁸ and Catalán and coworkers' SPP scale.¹⁹ Solvent-dependent spectral shifts are often analyzed in terms of such a single parameter. However, empirical single-parameter solvent scales regularly appear to be inappropriate because that specific parameter is so dependent on the particular probe used to construct the single-parameter scale concerned that it fails to predict the behavior of other solutes with considerably different properties from those of the probe.¹³ Multi-parameter approaches, which use multiple scales to describe specific and general solvent effects, have been applied successfully to various physicochemical properties.¹ However, a solvatochromic behavior which is exclusively caused by changes in solvent polarizability cannot be accurately described by e.g. the Kamlet, Abboud and Taft's π^* parameter because this parameter reflects the combined effect of solvent dipolarity and polarizability. To solve this problem, it is necessary to split the two contributions of the general solvent effect, namely solvent dipolarity and polarizability and, hence, to establish two corresponding, independent solvent scales for nonspecific solvent-solute interactions. This was done by Catalán, who proposed the generalized treatment of the solvent effect based on a set of four empirical, complementary, mutually independent solvent scales [for solvent polarizability (SP), dipolarity (SdP), acidity (SA) and basicity (SB),13 with corresponding weights c_{SP} , d_{SdP} , a_{SA} and b_{SB} (see eq 1)].

The detailed analyses of the spectroscopic maxima \overline{v}_{abs} and \overline{v}_{em} of BODIPYs **3–5** are given next. The results of the analyses are compiled in Table S7. From these analyses according to eq 1 with {SA, SB, SP, SdP}, three important conclusions can be drawn: (i) Solvent acidity (parameterized by SA) and basicity (parameterized by SB) have a negligible influence on the solvatochromic shifts of \overline{v}_{abs} and \overline{v}_{em} . (ii) For each dye, the values estimated for c_{SP} from the multilinear regression analyses of \overline{v}_{abs} and \overline{v}_{em} are always negative and have a comparable magnitude, but with a larger negative value from the \overline{v}_{em} analyses. (iii) For each dye, the values estimated for d_{SdP} from the multilinear regression analyses of \overline{v}_{abs} and \overline{v}_{em} are always positive with a larger negative value from the \overline{v}_{abs} analyses.

BODIPY 3

The relatively large estimates of $\{c_{SP}, d_{SdP}\}$ with concomitant comparatively small standard errors in relation to $\{a_{SA}, b_{SB}\}$ identify solvent polarizability and dipolarity as the more important parameters influencing the position of \overline{v}_{abs} of **3**. That solvent polarizability is more essential is derived from the four analyses of \overline{v}_{abs} according to eq 1, in which either SA, SB, SP, or SdP is left out as independent variable. Indeed,

the analysis with {SA, SB, SdP} as independent variables has the lowest *r*-value (0.753) vs. r = 0.983, 0.982 and 0.885 for the analyses with {SB, SP, SdP}, {SA, SP, SdP} and {SA, SB, SP}, respectively. Provided that SP is present as independent variable in the analyses according to eq 1 with two independent variables, excellent fits are obtained. This is found for the three analyses with {SA, SP}, {SB, SP} and {SdP, SP} yielding *r*-values of 0.862, 0.880 and 0.976, respectively. That the analysis with {SP, SdP} yields the best fit is further evidence for SP and to a lesser degree SdP as key solvent scales. Extra evidence that solvent polarizability is a key parameter for the solvent dependence of \overline{v}_{abs} is derived from the excellent fit of \overline{v}_{abs} vs. the Bayliss function²⁰ $f(n) = (n^2 - 1)/(2n^2 + 1)$, with r = 0.935.

Analogous analyses of \overline{v}_{em} according to eq 1 also point to solvent polarizability and to a lesser degree dipolarity as crucial factors determining the position of emission spectra. Exclusion of SP from the analysis (that is, with {SA, SB, SdP} as independent variables) yields a fit with the lowest *r*-value (0.624) vs. r = 0.978, 0.986 and 0.960 for the analyses with {SB, SP, SdP}, {SA, SP, SdP} and {SA, SB, SP} respectively. As long as SP is present as independent variable in the analyses according to eq 1 with two independent variables, excellent fits are obtained. This is found for the three analyses with {SA, SP}, {SB, SP} and {SdP, SP} yielding *r*values of 0.956, 0.959 and 0.976, respectively. Even the linear fit of \overline{v}_{em} vs. SP has an excellent correlation (r = 0.955), demonstrating that solvent polarizability determines mainly the spectroscopic shifts of \overline{v}_{em} . The excellent fit of \overline{v}_{em} vs. the Bayliss function (r = 0.975) confirms this.

BODIPY 4

In order to find out which solvent properties principally account for the shifts of \overline{v}_{abs} and \overline{v}_{em} of **4**, Catalán analyses according to eq 1 were carried out in which systematically one, two and three solvent scales were omitted. The results of the analyses of \overline{v}_{abs} and \overline{v}_{em} of **4** are very similar to those obtained for **3**. From this multitude of analyses, it is evident that solvent polarizability (and to a lesser degree solvent dipolarity) are primarily responsible for the observed shifts of \overline{v}_{abs} and \overline{v}_{em} .

BODIPY 5

Also for this dye, Catalán analyses according to eq 1 were carried out in which systematically one, two and three solvent scales were omitted in order to determine which solvent properties predominantly account for the shifts of $\bar{\nu}_{abs}$ and $\bar{\nu}_{em}$. The results of the analyses of $\bar{\nu}_{abs}$ and $\bar{\nu}_{em}$ of **5** are very similar to those obtained for **3** and **4**. From this collection of analyses, it is concluded that solvent polarizability (SP) and to a lesser extent solvent dipolarity (SdP) are principally accountable for the measured shifts of $\bar{\nu}_{abs}$ and $\bar{\nu}_{em}$.

Table S6. Estimated coefficients (y_0 , a_{SA} , b_{SB} , c_{SP} , d_{SdP} ; in cm⁻¹) and correlation coefficient (r) for the (multiple) linear regression analyses according to eq 1 of the absorption ($\overline{\nu}_{abs}$) and fluorescence emission maxima ($\overline{\nu}_{em}$) of **1** and **2** as a function of the Catalán solvent scales {SA, SB, SP, SdP} for the solvents listed in Tables 3 and S2. To highlight the differences of the c_{SP} and d_{SdP} estimates from the $\overline{\nu}_{abs}$ and $\overline{\nu}_{em}$ fitting according to eq 1, these values are displayed in red.

		<i>Y</i> 0	<i>a</i> _{SA}	$b_{ m SB}$	$\mathcal{C}_{\mathrm{SP}}$	$d_{\rm SdP}$	r
1	$\overline{\nu}_{abs}$	20936 ± 102	-189 ± 57	46 ± 45	-1266 ± 135	319 ± 31	0.984
	$\overline{\nu}_{abs}$	20855 ± 144		55 ± 65	-1133 ± 188	274 ± 41	0.962
	$\overline{\nu}_{abs}$	21004 ± 78	-193 ± 57		-1344 ± 112	325 ± 30	0.982
	$\overline{\nu}_{abs}$	20002 ± 70	-32 ± 177	282 ± 122		256 ± 98	0.791
	$\overline{\nu}_{abs}$	20858 ± 362	64 ± 182	132 ± 158	-962 ± 470		0.744
	$\overline{\nu}_{abs}$	20934 ± 108			-1223 ± 152	280 ± 39	0.959
	$\overline{\nu}_{abs}$	20125 ± 64	149 ± 204	306 ± 152			0.588
	$\overline{\nu}_{em}$	20755 ± 105	-125 ± 59	-43 ± 46	-1316 ± 140	163 ± 32	0.972
	$\overline{\nu}_{em}$	20701 ± 121		-37 ± 55	-1228 ± 157	134 ± 34	0.956
	$\overline{\nu}_{em}$	20692 ± 80	-122 ± 58		-1245 ± 115	158 ± 31	0.969
	$\overline{\nu}_{em}$	19783 ± 72	38 ± 184	203 ± 126		97 ± 102	0.583
	$\overline{\nu}_{em}$	20714 ± 204	4 ± 103	1 ± 89	-1161 ± 265		0.877
	$\overline{\nu}_{em}$	20716 ± 148	4 ± 98		-1162 ± 211		0.877
	$\overline{\nu}_{em}$	20716 ± 189		1 ± 84	-1163 ± 245		0.877
	$\overline{\nu}_{em}$	20648 ± 89			-1168 ± 126	130 ± 33	0.954
2	$\overline{\nu}_{abs}$	20261 ± 97	-125 ± 54	15 ± 43	-943 ± 129	244 ± 29	0.975
	$\overline{\nu}_{abs}$	20208 ± 115		21 ± 52	-856 ± 150	215 ± 32	0.957
	$\overline{\nu}_{abs}$	20284 ± 70	-126 ± 51		-969 ± 101	246 ± 28	0.974
	$\overline{\nu}_{abs}$	19566 ± 53	-8 ± 135	191 ± 93		197 ± 75	0.782
	$\overline{\nu}_{abs}$	20201 ± 283	69 ± 142	81 ± 123	-711 ± 367		0.720
	$\overline{\nu}_{abs}$	20239 ± 83			-890 ± 118	217 ± 30	0.956
	$\overline{\nu}_{em}$	17894 ± 143	41 ± 80	140 ± 63	201 ± 190	181 ± 43	0.899
	$\overline{\nu}_{em}$	17911 ± 133		138 ± 60	173 ± 173	190 ± 37	0.895
	$\overline{\nu}_{em}$	18099 ± 131	30 ± 95		-34 ± 188	199 ± 51	0.831
	$\overline{\nu}_{em}$	18042 ± 30	16 ± 77	103 ± 53		191 ± 43	0.884
	$\overline{\nu}_{em}$	17849 ± 239	184 ± 121	189 ± 104	374 ± 311		0.625
	$\overline{\nu}_{em}$	18073 ± 26				206 ± 42	0.827

Table S7. Estimated coefficients $(y_0, a_{SA}, b_{SB}, c_{SP}, d_{SdP}; \text{ in cm}^{-1})$ and correlation coefficient (r) for the (multiple) linear regression analyses according to eq 1 of the absorption $(\bar{\nu}_{abs})$ and fluorescence emission maxima $(\bar{\nu}_{em})$ of **3**, **4** and **5** as a function of the Catalán solvent scales {SA, SB, SP, SdP} for the solvents listed in Tables S3–S5. To highlight the differences of the c_{SP} and d_{SdP} estimates from the $\bar{\nu}_{abs}$ and $\bar{\nu}_{em}$ fitting according to eq 1, these values are displayed in red.

		<i>Y</i> 0	a _{SA}	$b_{\rm SB}$	$\mathcal{C}_{\mathrm{SP}}$	$d_{ m SdP}$	r
3	$\overline{\nu}_{abs}$	20558 ± 73	-81 ± 41	69 ± 32	-1180 ± 97	186 ± 22	0.989
	$\overline{\nu}_{abs}$	20524 ± 82		73 ± 37	-1123 ± 107	167 ± 23	0.983
	$\overline{\nu}_{abs}$	20660 ± 66	-86 ± 48		-1297 ± 95	195 ± 26	0.982
	$\overline{\nu}_{abs}$	19688 ± 64	66 ± 162	290 ± 111		127 ± 90	0.753
	$\overline{\nu}_{abs}$	20512 ± 215	66 ± 108	119 ± 94	-1003 ± 279		0.885
	$\overline{\nu}_{abs}$	20629 ± 70			-1243 ± 100	175 ± 26	0.976
	$\overline{\nu}_{em}$	20422 ± 78	-105 ± 44	26 ± 35	-1399 ± 104	97 ± 24	0.987
	$\overline{\nu}_{em}$	20377 ± 94		30 ± 43	-1326 ± 123	72 ± 27	0.978
	$\overline{\nu}_{em}$	20459 ± 58	-107 ± 42		-1442 ± 84	100 ± 23	0.986
	$\overline{\nu}_{em}$	19389 ± 75	69 ± 191	286 ± 132		27 ± 106	0.624
	$\overline{\nu}_{em}$	20398 ± 129	-28 ± 65	51 ± 56	-1307 ± 167		0.960
	$\overline{\nu}_{em}$	20420 ± 70			-1375 ± 98	75 ± 24	0.976
	$\overline{\nu}_{em}$	20461 ± 89			-1374 ± 129		0.955
4	$\overline{\nu}_{abs}$	20276 ± 77	-55 ± 43	106 ± 34	-1023 ± 102	181 ± 23	0.987
	$\overline{\nu}_{abs}$	20408 ± 80			-1162 ± 113	179 ± 29	0.967
	$\overline{\nu}_{em}$	20075 ± 120	-29 ± 67	11 ± 53	-1156 ± 159	142 ± 37	0.963
	$\overline{\nu}_{em}$	20080 ± 80			-1155 ± 114	137 ± 29	0.962
5	$\overline{\nu}_{abs}$	20798 ± 79	-91 ± 44	23 ± 35	-1096 ± 105	214 ± 24	0.985
	$\overline{\nu}_{abs}$	20798 ± 66			-1075 ± 94	196 ± 24	0.976
	$\overline{\nu}_{em}$	20427 ± 181	-88 ± 101	-13 ± 80	-1177 ± 240	172 ± 55	0.920
	$\overline{\nu}_{em}$	20376 ± 125			-1101 ± 177	150 ± 46	0.912

Density Functional Theory (DFT) Calculated Emission Spectra (from

Ab Initio Molecular Dynamics)

All DFT calculations were performed at the University of Nottingham (United Kingdom).



Figure S7-a. Calculated gas-phase emission spectra (in eV) of 1, 2 and 3, using DFT (B3LYP/6-311G*).



Figure S7-b. Calculated gas-phase emission spectra (in nm) of **1**, **2** and **3**, using DFT (B3LYP/6-311G*).



Figure S8-a. Calculated emission spectra (in eV) of 1, 2 and 3 in CH_2Cl_2 , using DFT (B3LYP/6-311G*).



Figure S8-b. Calculated emission spectra (in nm) of 1, 2 and 3 in CH_2Cl_2 , using DFT (B3LYP/6-311G*).

¹H and ¹³C NMR Spectra of 1–5 and 7





S24







S26



BODIPY 4



BODIPY 5









References

- B. Valeur, B.; M. N. Berberan-Santos, M. N. *Molecular Fluorescence. Principles and Applications*, 2nd ed., Wiley-VCH: Weinheim (Germany), 2012.
- (2) Lakowicz, J. Principles of Fluorescence Spectroscopy, 3rd ed., Springer-Verlag: New York, 2006.
- (3) Olmsted, J. Calorimetric Determinations of Absolute Fluorescence Quantum Yields. J. Phys. Chem. 1979, 83, 2581–2584.
- (4) Becker, W. Advanced Time-Correlated Single Photon Counting Techniques, Springer Series in Chemical Physics, Vol. 81, Springer: Berlin, 2005.
- (5) vandeVen, M.; Ameloot, M.; Valeur, B.; Boens, N. Pitfalls and Their Remedies in Time-Resolved Fluorescence Spectroscopy and Microscopy. J. Fluoresc. 2005, 15, 377–413.
- (6) Boens, N.; Qin, W.; Basarić, N.; Hofkens, J.; Ameloot, M.; Pouget, J.; Lefèvre, J. P.; Valeur, B.; Gratton, E.; Vandeven, M.; Silva, N. D. Jr.; Engelborghs, Y.; Willaert, K.; Sillen, A.; Rumbles, G.; Phillips, D.; Visser, A. J. W. G.; van Hoek, A.; Lakowicz, J. R.; Malak, H.; Gryczynski, I.; Szabo, A. G.; Krajcarski, D. T.; Tamai, N.; Miura, A. Fluorescence Lifetime Standards for Time and Frequency Domain Fluorescence Spectroscopy. *Anal. Chem.* 2007, *79*, 2137–2149.
- (7) Lemmetyinen, H.; Tkachenko, N. V.; Valeur, B.; Hotta, J.-i.; Ameloot, M.; Ernsting, N. P.; Gustavsson, T.; Boens, N. Time-Resolved Fluorescence Methods. *Pure Appl. Chem.* 2014, *86*, 1969–1998.
- (8) SMART, Version 5.0, Bruker AXS, Madison, WI, USA, 1998.
- (9) SAINT Version 6.0, Bruker AXS, Madison, WI, USA, 1999.
- (10) Sheldrick, G. M. SHELXL-97, Program for X-ray Crystal Structure Solution, University of Gottingen (Germany), 1997.
- (11) SHELXTL Version 5.10, Program Library for Structure Solution and Molecular Graphics, Bruker AXS, Madison, WI, 1998.
- (12) Vos de Wael, E.; Pardoen, J. A.; van Koeveringe, J. A.; Lugtenburg, J. Pyrromethene-BF₂ Complexes (4,4'-difluoro-4-bora-3a,4a-diaza-s-indacenes). Synthesis and Luminescence Properties. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 306–309.
- (13) Catalán, J. Toward a Generalized Treatment of the Solvent Effect Based on Four Empirical Scales: Dipolarity (SdP, a New Scale), Polarizability (SP), Acidity (SA), and Basicity (SB) of the Medium. J. Phys. Chem. B 2009, 113, 5951–5960.
- (14) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. Über Pyridinium-*N*-phenol-betaine und ihre Verwendung zur Charakterisierung der Polarität von Lösungsmitteln (Pyridinium-*N*-phenolbetaine and its Application for the Characterization of Solvent Polarities). *Liebigs Ann. Chem.* **1963**, *661*, 1–37.
- (15) Dimroth, K.; Reichardt, C. Über Pyridinium-*N*-phenol-betaine und ihre Verwendung zur Charakterisierung der Polarität von Lösungsmitteln, V Erweiterung der Lösungsmittelpolaritätsskala durch Verwendung Alkyl-substituierter Pyridinium-*N*-phenolbetaine (Pyridinium-*N*-phenol Betaines and Their Application for the Characterization of Solvent Polarities. Extension of the Solvent Polarity Scale by Application of Alkyl-substituted Pyridinium-*N*-phenol Betaines). *Liebigs Ann. Chem.* **1969**, *727*, 93–105.
- (16) Reichardt, C. Solvatochromism, Thermochromism, Piezochromism, Halochromism, and Chirosolvatochromism of Pyridinium *N*-phenoxide Betaine Dyes. *Chem. Soc. Rev.* **1992**, *21*, 147–153.

- (17) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. The Solvatochromic Comparison Method. 6. The π^* Scale of Solvent Polarities. *J. Am. Chem. Soc.* **1977**, *99*, 6027–6038.
- (18) Dragos, R. S. Extension of the Unified Scale of Solvent Polarities to Acceptor Probes: Concerns about β - π * Parameters. *J. Org. Chem.* **1992**, *57*, 6547–6552.
- (19) Catalán, J.; López, V.; Pérez, P.; Martin-Villamil, R.; Rodriguez, J. G. Progress Towards a Generalized Solvent Polarity Scale: The Solvatochromism of 2-(Dimethylamino)-7-nitrofluorene and its Homomorph 2-Fluoro-7-nitrofluorene. *Liebigs Ann.* **1995**, 241–252.
- (20) N. S. Bayliss, J. Chem. Phys., 1950, 18, 292-296.