Supporting Information

UV–vis Spectroscopy of the Coupling Products of the Palladium-Catalyzed C–H Arylation of the BODIPY Core

Lina Wang,[a] Bram Verbelen,[a] Claire Tonnelé,[b] David Beljonne,[b] Roberto Lazzaroni,[b] Volker Leen,[a] Wim Dehaen,[a] Noël Boens [a, *]

[a] *Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200f – bus 02404, 3001 Leuven, Belgium.*

[b] *Laboratory for Chemistry of Novel Materials, Université de Mons, Place du Parc 20, 7000 Mons, Belgium.*

Contents

----

* Corresponding author: Tel.: +32-16-327497, Fax: +32-16-327990, E-mail: Noel.Boens@chem.kuleuven.be
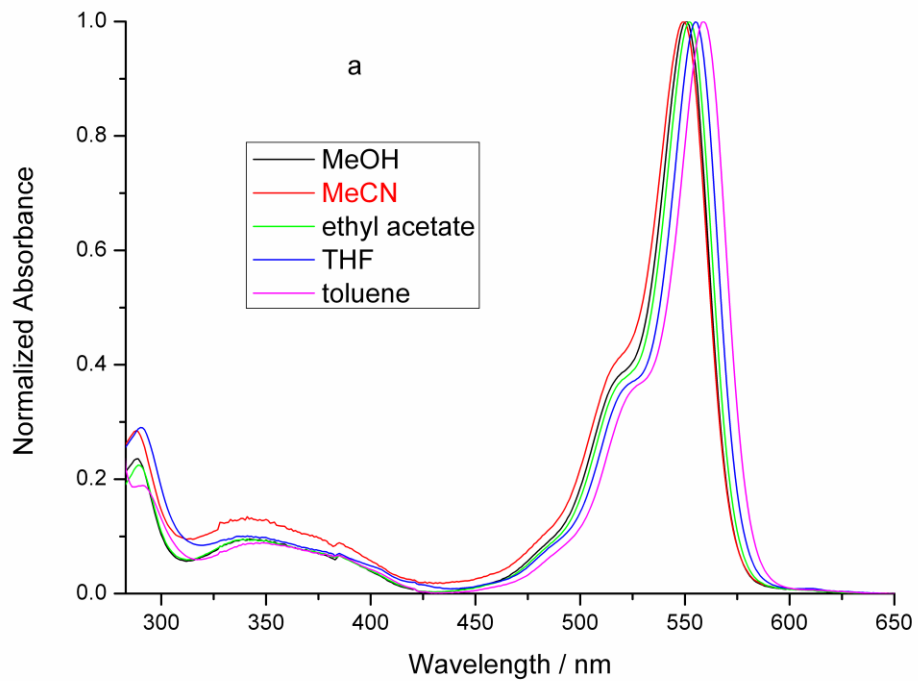
Fig. S1. Normalized UV–vis absorption spectra of **5** in the solvents indicated. Note the narrow, optically near-transparent window centered around 430 nm.

Fig. S2. (a) Normalized, visible absorption spectra of **6** in the solvents indicated. (b) Corresponding normalized fluorescence emission spectra upon excitation at 560 nm.
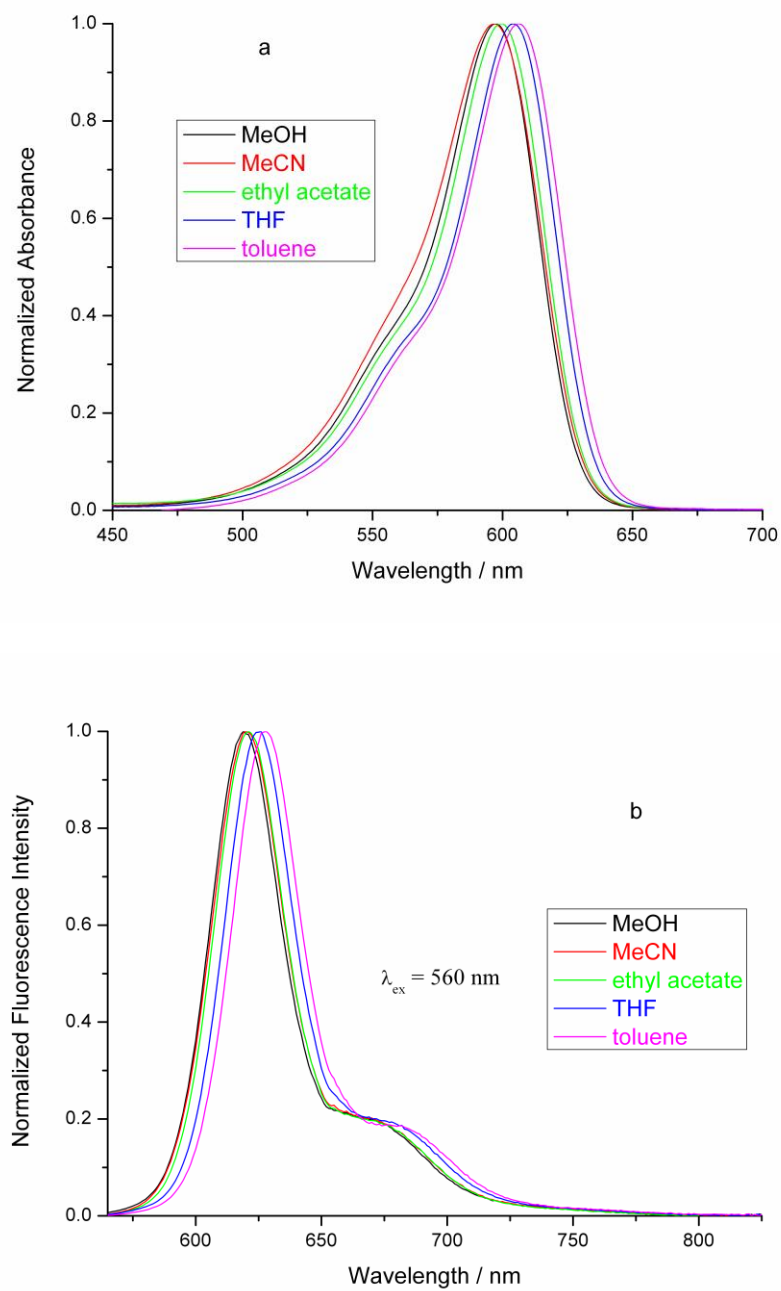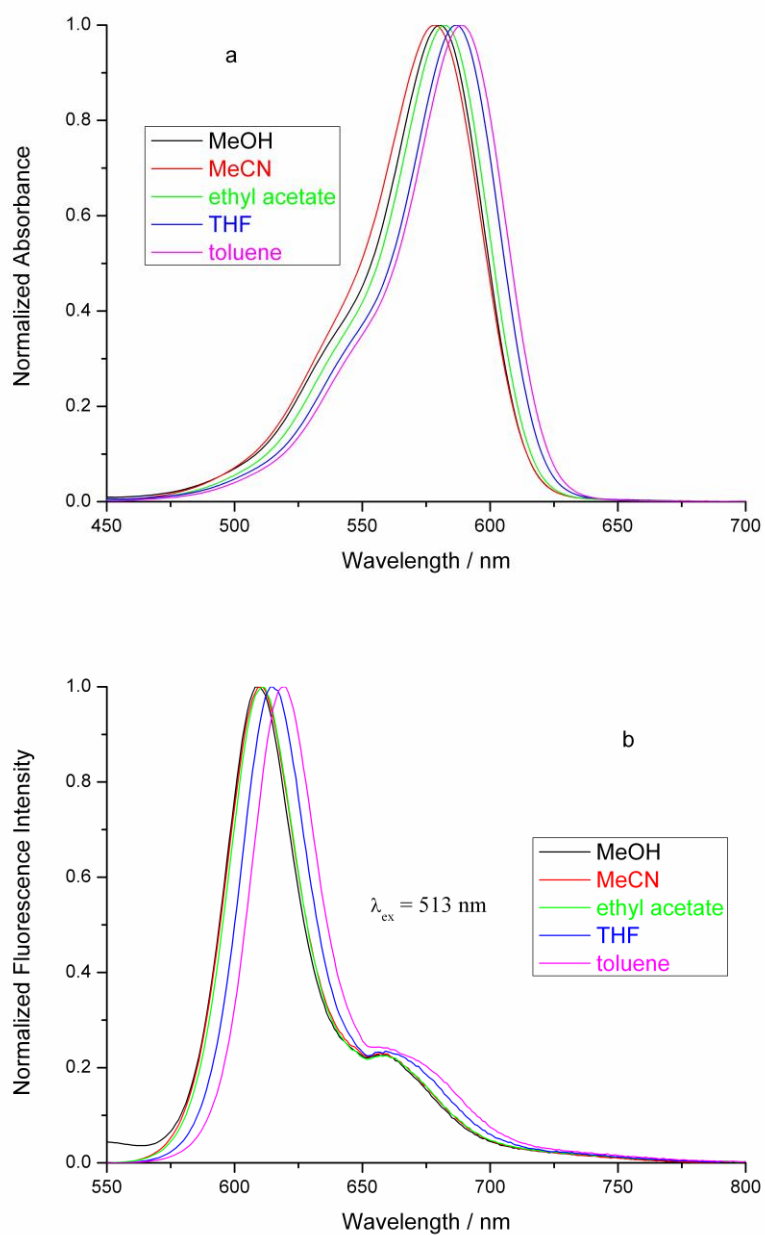
Fig. S3. (a) Normalized, visible absorption spectra of **14** in the solvents indicated. (b) Corresponding normalized fluorescence emission spectra upon excitation at 513 nm.

Solvatochromism

As shown in Table 1 and Figs. 1, 2, S1–S3, the influence of the solvent on λ_{abs}(max) and λ_{em}(max) is minimal. It is worthwhile to determine the cause of these small solvent-dependent changes.

The solvent effect can be divided into specific (donor-acceptor and acid-base) interactions and nonspecific (arising from the solvent acting as a dielectric continuum) interactions. These interactions have been empirically parameterized by a sizable collection of solvent scales [see ref. 1 for an overview of solvent scales (or parameters) proposed in the literature]. 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 $E_T(30)$,[2] Kamlet, Abboud and Taft's π^* parameter,[3] Dragos' S' scale,[4] and Catalán and coworkers' SPP scale.[5] 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.[1] Multi-parameter approaches, which use multiple scales to describe specific and general solvent effects, have been applied successfully to various physicochemical properties.[6] 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.

Consequently, the generalized treatment of the solvent effect based on a set of four empirical, complementary, mutually independent solvent scales was recently proposed by Catalán.[1] In this method, the polarizability and dipolarity of a particular solvent are characterized by the parameters SP[7] and SdP,[1] respectively, whereas acidity and basicity are described by the scales SA[8, 9] and SB[10], respectively (eq S1). The {SA, SB, SP, SdP} parameters for a large number of solvents can be found in ref 1. Mathematically, the solvent effect on the physicochemical observable y can be expressed by the multi-linear equation S1:

$$y = y_0 + a_{SA}\, SA + b_{SB}\, SB + c_{SP}\, SP + d_{SdP}\, SdP \tag{S1}$$

where y_0 denotes the physicochemical property of interest in the gas phase; a_{SA}, b_{SB}, c_{SP} and d_{SdP} are regression coefficients that reflect the sensitivity of the observable y to the various solvent-solute interaction mechanisms; and {SA, SB, SP, SdP} are independent solvent parameters accounting for various types of solvent-solute interactions.

The spectroscopic observables y analyzed in this paper are the absorption maxima $\bar{\nu}_{abs} = 1/\lambda_{abs}$(max) and the emission maxima $\bar{\nu}_{em} = 1/\lambda_{em}$(max) of **5**, both expressed in cm^{-1}.

Use of the Catalán solvent parameter set {SA, SB, SP, SdP} – where solvent dipolarity and polarizability effects are split – gives high-quality fits to $\bar{v}_{abs}$ of **5** using r as goodness-of-fit criterion (eq S2 with n = 12 (n denotes the number of data points) and r = 0.957).

$$\bar{v}_{abs} = (18993 \pm 263) - (63 \pm 78)SA - (111 \pm 101)SB - (1405 \pm 298)SP + (125 \pm 57)\ SdP \tag{S2}$$

These excellent regression analysis results can be compared to those obtained using the popular Kamlet-Taft solvent scales using {α, β, π^*}, for which an unsatisfactory fit is found, as judged by the lower r-value (0.762).

Excellent fits were also found for the multi-linear analysis of the $\bar{v}_{em}$ data of **5** with the {SA, SB, SP, SdP} parameter set (eq S3 with n = 12 and r = 0.967).

$$\bar{v}_{em} = (18248 \pm 220) - (23 \pm 65)SA + (31 \pm 85)SB - (1081 \pm 250)SP + (121 \pm 48)\ SdP \tag{S3}$$

Contrary to these superb results, the Kamlet–Taft approach with the {α, β, π^*} parameters is not as successful in describing the $\bar{v}_{em}$ data of **5** (r = 0.831). It is remarkable that the small solvent-dependent spectral shifts (all $\bar{v}_{abs}$ are located within 358 cm^{-1}, the difference between maximal and minimal $\bar{v}_{em}$ amounts to 308 cm^{-1}) can be described so well by the new Catalán solvent scales. The added benefit of this generalized treatment of the solvent effect is that it allows one to separate the relative contributions of dipolarity, polarizability, acidity and basicity of the medium. As mentioned above, in the Kamlet–Taft approach, the solvent parameter π^* combines solvent dipolarity and polarizability effects, and hence, this methodology can never be utilized to entangle solvent polarizability and dipolarity effects.

Now we use the Catalán methodology to unravel which solvent property is primarily responsible for the observed spectral shifts. The very large (negative) estimated c_{SP} value compared to the {a_{SA}, b_{SB}, d_{SdP}} estimates in the analysis of $\bar{v}_{abs}$ and the relatively large standard errors on {a_{SA}, b_{SB}, d_{SdP}} in comparison to those on c_{SP} (eqs S1, S2) indicate that the small change of $\bar{v}_{abs}$ may reflect principally a change in polarizability of the environment of the chromophore. Further supporting evidence for this derives from the analyses of $\bar{v}_{abs}$ according to eq S1 in which one independent variable is omitted. Provided that SP (i.e., solvent polarizability) is included in the analysis, the r-value remains high (r = 0.926, 0.953 and 0.949 for the analyses with {SA, SB, SP}, {SB, SP, SdP} and {SA, SP, SdP} as independent variables, respectively). Conversely, the analysis, in which SP is left out, has the lowest r-value (0.805). That specific interactions (parameterized by {SA, SB}) have little to no influence on the position of $\bar{v}_{abs}$ is evidenced by the good description of the absorption data by eq S4. Indeed, the r-value for eq S4 (0.945, n = 12) is only fractionally lower than that for eq S2 (0.957), in which all four solvent parameters {SA, SB, SP, SdP} are utilized. However, the (minor) importance of solvent dipolarity (SdP) as factor determining the position of $\bar{v}_{abs}$ cannot be totally disregarded. Indeed, if a simple linear regression of $\bar{v}_{abs}$ as a function of SP is

performed, the *r*-value drops further to 0.881 compared to eq S4. However, solvent polarity should not be overrated either: the simple linear regression, of $\bar{\nu}_{abs}$ as a function of SdP yields $r = 0.599$. To summarize, solvent polarizability is the most crucial solvent property affecting $\bar{\nu}_{abs}$, although solvent polarity cannot be ignored.

$$\bar{\nu}_{abs} = (18717 \pm 126) - (1095 \pm 163)\,SP + (143 \pm 45)\,SdP \qquad (S4)$$

Furthermore, an excellent linear correlation is found between $\bar{\nu}_{abs}$ and $f(n^2) = (n^2 - 1)/(2n^2 + 1)$ ($r = 0.947$, Fig. S4), indicating that van der Waals and excitonic interactions with a polarizable solvent can rationalize to a large degree (but not exclusively) the solvent dependence of the excitation energy.[11] If a large difference in permanent dipole moment would exist between the ground and excited state, the excitation energy would depend linearly on the Lippert solvent parameter $\Delta f = f(\varepsilon) - f(n^2) = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$ rather than on $f(n^2)$ alone and hence no linear dependence on $f(n^2)$ would be observed anymore.

Now we investigate which solvent property principally accounts for the shifts of $\bar{\nu}_{em}$. The relatively large (negative) c_{SP} estimate and the rather large standard errors on $\{a_{SA}, b_{SB}, d_{SdP}\}$ in comparison to those on c_{SP} (eq S3) point to solvent polarizability as key factor affecting $\bar{\nu}_{em}$. The analyses of $\bar{\nu}_{em}$ according to eq S1 with {SA, SB, SP}, {SB, SP, SdP} and {SA, SP, SdP} as independent variables (the common independent variable in all these analyses is SP) all gave high-quality fits ($r = 0.935$, 0.966 and 0.966, respectively). Comparison of these three regression analyses shows that the highest *r*-values (0.966) are found when SP (solvent dipolarity) and SdP (solvent polarizability) are both present in the analyses, implying the importance of these solvent parameters. The analyses of $\bar{\nu}_{em}$ according to eq S1, in which SP was disregarded (i.e., with {SA, SB, SdP} as independent variables), gave a lower *r*-value (0.872). Specific interactions (parameterized by {SA, SB}) have negligible influence on the position of $\bar{\nu}_{em}$ as corroborated by the excellent description of the emission data by eq S5. Indeed, the *r*-value for eq S5 (0.966, n = 12) is nearly the same as for eq S3 (0.967, n = 12). The simple linear regressions of $\bar{\nu}_{em}$ versus SP and SdP yield *r*-values of 0.927 and 0.544, respectively, confirming that solvent polarizability is by far the most crucial parameter influencing $\bar{\nu}_{em}$, with solvent dipolarity as minor factor. Supplementary evidence that the position of $\bar{\nu}_{em}$ is controlled mainly by solvent polarizability comes from the excellent linear correlation between $\bar{\nu}_{em}$ and $f(n^2)$ ($r = 0.978$, Fig. S4). The linearity of the plot of $\bar{\nu}_{em}$ versus $f(n^2)$ confirms that van der Waals and excitonic interactions with a polarizable solvent are primarily responsible for the experimentally observed solvent-dependent shifts of $\bar{\nu}_{em}$.[11]

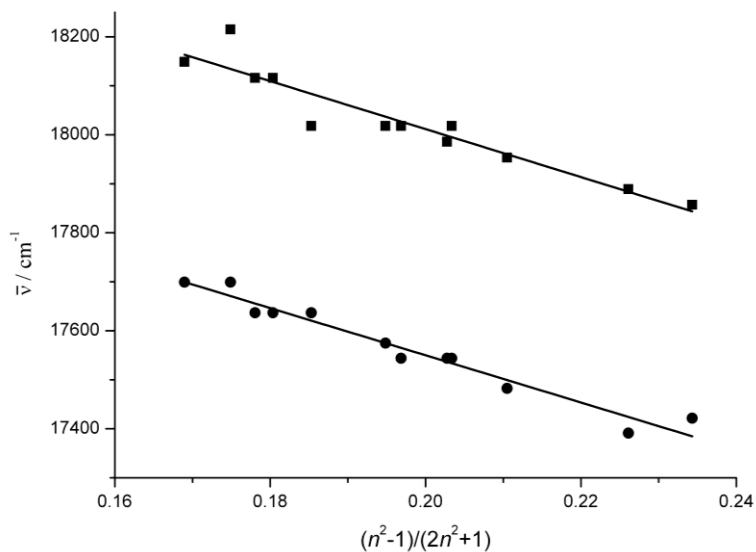$$\bar{\nu}_{em} = = (18307 \pm 96) - (1139 \pm 124)\,SP + (108 \pm 35)\,SdP \qquad (S5)$$

Fig. S4. Plots of the absorption maxima ($\overline{\nu}_{abs}$, solid squares) and fluorescence emission maxima ($\overline{\nu}_{em}$, solid circles) for compound **5** *vs.* $f(n^2) = (n^2 - 1)/(2n^2 + 1)$ as a function of solvent (n denotes the refractive index of the solvent). The straight lines represent the best linear fits to the data ($r = 0.947$ for $\overline{\nu}_{abs}$ and $r = 0.978$ for $\overline{\nu}_{em}$).

HOMO   LUMO
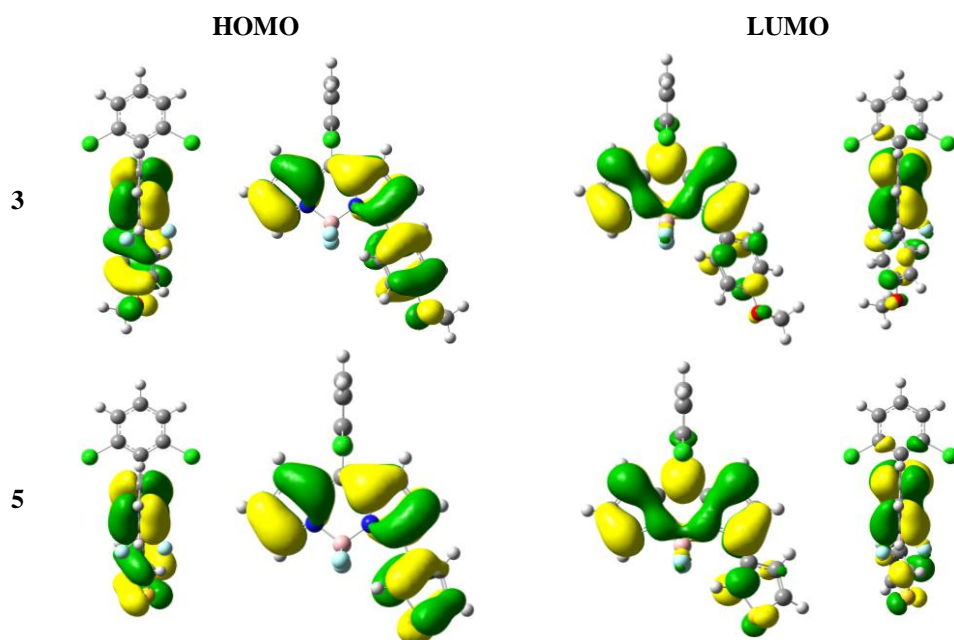
3

5

Fig. S5. Graphical representation of the frontier orbitals of **3** (up) and **5** (down).
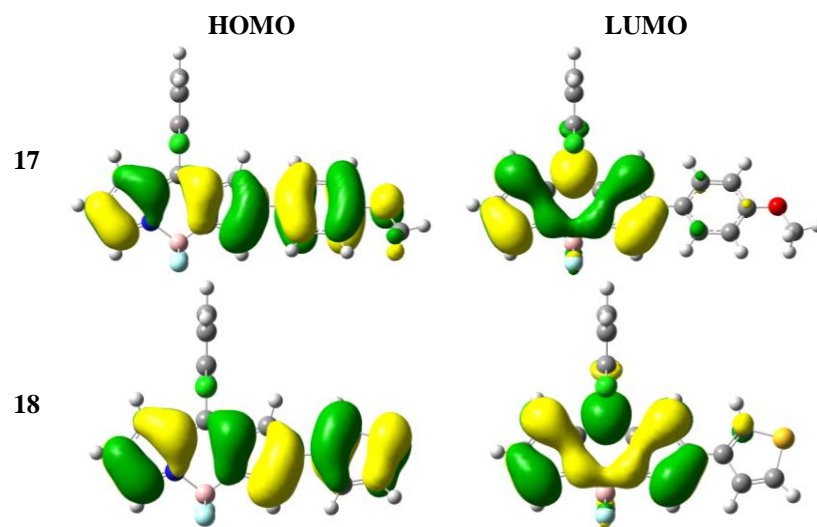
HOMO   LUMO

17

18

Fig. S6. Graphical representation of the frontier orbitals of **17** (up) and **18** (down).

Steady-state spectroscopy – Determination of molar absorption coefficient ε(λ)

The electronic absorption spectra and absorbances were measured at 20 °C on a Perkin-Elmer Lambda 40 UV–vis spectrophotometer. Corrected steady-state excitation and emission spectra were recorded on a Spex Fluorolog instrument with temperature-controlled cell holder. Freshly prepared samples in 1 cm quartz cells were used to perform all UV–vis absorption and fluorescence measurements. For each dye in a specific solvent, multiple (between 3 and 6) absorption and fluorescence spectra were measured as a function of concentration. Because the spectra are recorded digitally and the peaks are relatively narrow, the maxima λ_{abs}(max) and λ_{em}(max) can be determined not only by visual inspection, but also from the digital data and the analysis-calculus-integrate menu of the Origin software. The standard uncertainty on λ_{abs}(max) and λ_{em}(max) is approximately 1 nm.

For the determination of the molar absorption coefficient ε(λ) of a specific BODIPY dye in a particular solvent at wavelength λ, the next protocol was followed.
(1). A stock solution was prepared by dissolving a weighed amount of the dye in the solvent of choice.
(2). Subsequently, from this stock solution several dilutions (usually ≥ 5) were prepared.
(3). The absorbance A of the different solutions were measured. To obtain consistent A values, we prefer to record a small portion of the spectrum centered around λ instead of measuring A at a single, preset wavelength λ. To minimize errors on A, the values of A should be neither too small nor too large. Therefore, we generally use A values between 0.1 and 1.0.
(4). For this series, the absorbance A *vs*. concentration c data were analyzed *via* linear regression. The equation $A = a\,c + b$ algebraically describes a straight line for a set of data with one independent variable where c (concentration) is the independent variable, A (absorbance) is the dependent variable, a represents the slope of the line and b represents the A-intercept. When using 1 cm optical path length cuvettes, the recovered regression coefficient a (slope) equals the estimated value of ε(λ) at wavelength λ (Beer-Lambert law). The estimated regression coefficient (intercept) b should be very close to zero.
(5). Then a second stock solution was made by weighing and dissolving a different amount of the dye.
(6). Again several dilutions were prepared and
(7) their absorbance A measured.
(8). The linear least-squares analysis of this second series of {A, c} data provides estimates for ε(λ) (provided 1 cm cells are used) and b. Again, the b coefficient should be close to zero. The recovered ε(λ) values from these two individual, linear least-squares analyses should be equal within one standard error, or, in other words, the best-fit linear regression lines should nearly overlap.
(9) If this is the case, the final linear least-squares analysis of all concatenated {A, c} data yields the ε(λ) estimates, which are reported in this paper.
(10). However, if excessive discrepancies between the results from the two individual least-squares analyses are found, the whole protocol should be repeated.

The correlation coefficient squared, r^2, of the final, linear regression analyses reported here was in all cases higher than 0.998.

Relative determination of fluorescence quantum yield Φ

For the relative determination of the fluorescence quantum yield Φ of **1**–**15** in a series of solvents, the following formula (eq S6) was used:

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1-10^{-A_r(\lambda_{ex})}}{1-10^{-A_x(\lambda_{ex})}} \times \frac{n_x^2}{n_r^2} \tag{S6}$$

The subscripts x and r refer respectively to sample x (i.e., BODIPYs **1**–**15**) 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}, and 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 10 mm optical path length cuvettes under right-angle (L-) arrangement and 'magic angle' conditions. Cresyl violet in methanol (Φ = 0.55) and rhodamine 6G in methanol (Φ = 0.86) were used as fluorescence quantum yield references. All measurements were done on non-degassed samples at 20 °C. The averages and standard uncertainties of Φ reported in Table 1 are computed from 12 independent Φ measurements, resulting from 3 conc. of sample x × 2 conc. of reference r × 2 excitation wavelengths λ_{ex}.

References

(1) J. Catalán, 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.

(2) (a) K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, Über Pyridinium-*N*-phenol-betaine und ihre Verwendung zur Charakterisierung der Polarität von Lösungsmitteln, *Liebigs Ann. Chem.*, 1963, **661**, 1–37. (b) K. Dimroth and C. Reichardt, Über Pyridinium-*N*-phenol-betaine und ihre Verwendung zur Charakterisierung der Polarität von Lösungsmitteln, Verweiterung der Lösungsmittelpolaritätsskala durch Verwendung Alkyl-substituierter Pyridinium-*N*-phenol-betaine, *Liebigs Ann. Chem.*, 1969, **727**, 93–105. (c) C. Reichardt, Solvatochromism, Thermochromism, Piezochromism, Halochromism, and Chiro-solvatochromism of Pyridinium *N*-phenoxide Betaine Dyes, *Chem. Soc. Rev.*, 1992, **21**, 147–153.

(3) M. J. Kamlet, J. L. Abboud and R. W. Taft, The solvatochromic comparison method. 6. The π^* scale of solvent polarities, *J. Am. Chem. Soc.*, 1977, **99**, 6027–6038.

(4) R. S. Dragos, Extension of the Unified Scale of Solvent Polarities to Acceptor Probes: Concerns about $\beta-\pi^*$ Parameters, *J. Org. Chem.*, 1992, **57**, 6547–6552.

(5) J. Catalán, V. López, P. Pérez, R. Matin-Villamil and J. G. Rodriguez, 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.

(6) B. Valeur and M. N. Berberan-Santos, *Molecular fluorescence. Principles and applications*, Wiley-VCH, Weinheim (Germany), 2nd ed., 2012.

(7) J. Catalán and H. Hopf, Empirical Treatment of the Inductive and Dispersive Components of Solute−Solvent Interactions: The Solvent Polarizability (SP) Scale, *Eur. J. Org. Chem.*, 2004, 4694−4702.

(8) J. Catalán, in *Handbook of solvents*, Wypych, G. Ed.; ChemTec Publishing, Toronto, 2001; pp 583−616.

(9) J. Catalán and C. Díaz, A Generalized Solvent Acidity Scale: The Solvatochromism of *o-tert*-Butylstilbazolium betaine Dye and Its Homomorph *o,o′*-Di-*tert*-butylstilbazolium Betaine Dye, *Liebigs Ann.*, 1997, 1941–1949.

(10) J. Catalán, C. Díaz, V. López, P. Pérez, J.-L. G. de Paz and J. G. Rodríguez, A Generalized Solvent Basicity Scale: The Solvatochromism of 5-Nitroindoline and Its Homomorph 1-Methyl-5-nitroindoline, *Liebigs Ann.*, 1996, 1785–1794.

(11) D. Pevenage, D. Corens, W. Dehaen, M. Van der Auweraer and F. C. De Schryver, Influence of the N-Substituent on the Photophysical Properties of Oxacarbocyanine Dyes in Solution, *Bull. Soc. Chim. Belg.*, 1997, **106**, 565−572.