Core-Substituted Naphthalene Bisimides: New Fluorophors with Tunable Emission Wavelength for FRET Studies**

Frank Würthner,*[a] Shahadat Ahmed,[a] Christoph Thalacker,[a] and Tony Debaerdemaeker[b]

Dedicated to Professor David N. Reinhoudt on the occasion of his 60th birthday

Abstract: Highly colored and photoluminescent naphthalene bisimide dyes have been synthesized from 2,6-dichloronaphthalene bisanhydride **1** by means of a stepwise nucleophilic displacement of the two chlorine atoms by alkoxides and/or alkyl amines. The alkoxy-substituted derivatives are yellow dyes with green emission and low photoluminescence quantum yields, whereas the amine-substituted derivatives exhibit a color range from red to blue with strong photoluminescence up to 76%. Structure–property relationships for this class of two-dimensional chromophores were evaluated based on a single-crystal X-ray analysis for dye **5a**, the observed solvatochromism, and quantum-chemical calculations. Owing to the simple tuning of the absorption properties over the whole visible range by the respective substituents, the pronounced brilliancy, and the intense photoluminescence, this class of dyes is considered to be highly suited for numerous applications such as fluorescent labeling of biomacromolecules and light-harvesting in supramolecular assemblies. As an important step towards such applications efficient FRET (fluorescence resonance energy transfer) has been demonstrated for a covalently tethered bichromophoric compound that contains a red and a blue naphthalene bisimide dye.

Keywords: chromophores · dyes/pigments · fluorescence · FRET (fluorescence resonance energy transfer) · nucleophilic substitution

Introduction

Despite the multitude of available dyes there is ongoing interest in new chromophoric systems that satisfy the special demands of emerging technologies which are often at the borders to biological[1] and physical sciences.[2] For example, new interest in fluorophors with long-wavelength emission has arisen in conjunction with single-molecule spectroscopy of biomolecules[3] where most traditional dyes lack the required fluorescence quantum yield and photostability or whose performance is hampered by aggregation of their extended π-conjugated cores. The second point holds especially true for one of the most useful families of dyes, the rylenes, which proved to be ideally suited for single-molecule spectroscopy owing to their high fluorescence quantum yields and photostability.[4, 5] Thus terrylene became one of the most applied dyes in this field[4] and perylene, terrylene, and quaterrylene bisimide dyes synthesized by the groups of Müllen and Langhals opened new possibilities.[5, 6] However, as a significant drawback these dyes exhibit extended π systems that are difficult to solubilize and exhibit a high tendency for the undesired formation of dye aggregates.[7] On the other hand, the smallest representative of the rylene bisimides, naphthalene bisimide, exhibits a colorless nonfluorescent π system that has been extensively applied in supramolecular chemistry,[8] DNA intercalation,[9] electrically conductive aggregates,[10] and recently as the active layer of organic field effect transistors.[11]

Herein we report on colored *and* fluorescent naphthalene 1,4,5,8-tetracarboxylic acid bisimides. We will show that core substitution with electron-donor groups allows the optical properties to be tuned over a wide spectral range and high fluorescence quantum yields to be obtained that—together with the easy access to these dyes—should open exciting new opportunities for the above-mentioned fields of research. Notably, these versatile fluorophors became available by means of a simple modification of dyes reported a long time ago by Vollmann et al.,[12] that is replacement of

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[**] FRET = fluorescence resonance energy transfer.

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arylamines with alkyl amines in the 2- and/or 6-position of naphthalene bisimides. These alkylamino-substituted derivatives exhibit brilliant colors and intense fluorescence, whereas Vollmann's arylamino-substituted derivatives are dull and nonfluorescent,[13] which might be the reason why this class of chromophores did not receive much attention to date.[14]

Results and Discussion

Synthesis: Following Vollmann's method 2,6-disubstituted naphthalene-1,4,5,8-tetracarboxylic acid bisimides were prepared as outlined in Scheme 1. Under acidic conditions 2,6-dichloronaphthalene bisanhydride reacted selectively with aryl (as well as alkyl)[13] amines at the anhydride carbonyl groups to yield bisimide **2**. Further reaction with nucleophilic alkoxides or amines under mild conditions in protic or dipolar aprotic solvents afforded the highly colored products **3**–**7**. Remarkably, the second chlorine atom of **2** is less readily exchanged than the first one thus allowing a stepwise nucleophilic displacement of the two chlorine atoms to give the red dyes **5a** and **5b** or the blue dye **7** just by increasing the concentration of the nucleophile and/or the reaction temperature. Likewise dyes bearing one alkoxy substituent may be prepared easily as demonstrated with **3** and **6** (Scheme 1).

Optical properties: All these naphthalene bisimides are isolated as colored solids with yellow (**4**), red (**5**), magenta (**6**), and blue (**7**) hues. From the UV/Vis absorption spectra in Figure 1 we see that each dye exhibits two intense absorption bands, one at 350 nm that is not influenced by the 2,6 substituents and another one that is shifted through the whole visible range, which is indicative of a strong electronic interaction between the naphthalene core and the respective substituents. The absorption maxima are located at about 470 nm for the yellow dye **4** bearing two alkoxy substituents, at 530 nm for the red dye **5** bearing one amine and one chlorine substituent, and at 620 nm for the blue dye **7** bearing two amino substituents (Table 1). This suggests that the electron-donating character (+*M* effect) is of paramount importance for the position of this absorption band similar to the situation in merocyanines dyes.[15] However, the bathochromic shift arising from the substituent is much larger than for merocyanine dyes (from the alkoxy dye **4** to the alkylamino derivative **7** we calculate a bathochromic shift of $\Delta\lambda = 151$ nm or $\Delta\tilde{\nu} = 5200\ \mathrm{cm}^{-1}$) and the band shape remains almost unchanged (in contrast to merocyanines[15b]). Another important coloristic effect arises from the unaltered position of the high-energy transition in the UV spectrum at $\lambda < 380$ nm; because this transition does not move into the visible range high brilliancy of all dyes is realized owing to a single absorption band in the visible range (Figure 1).

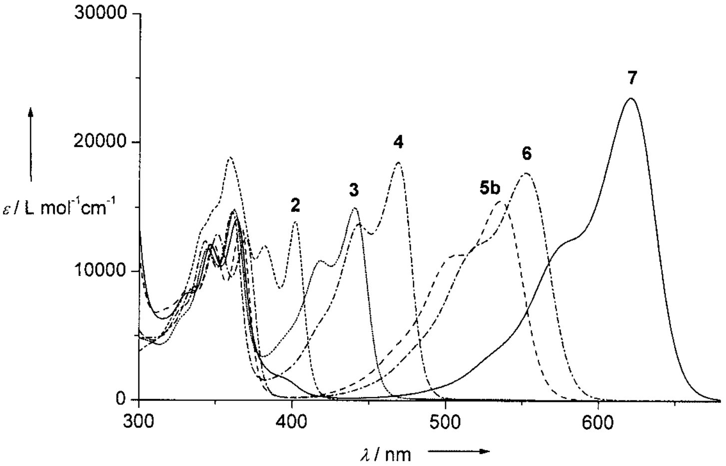
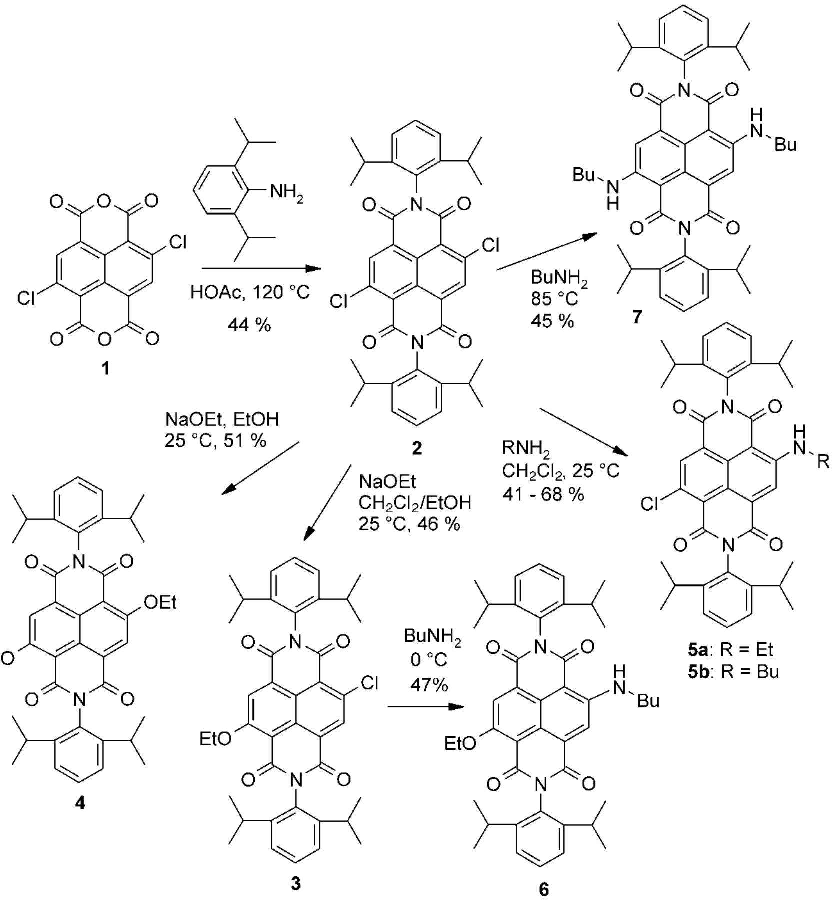


Figure 1. UV/Vis absorption spectra of dyes **2**–**7** in dichloromethane.



Scheme 1. Synthesis of naphthalene bisimide dyes **3**–**7**.

Table 1. Optical properties of naphthalene bisimides **2**–**7** in dichloromethane.

	Color[a] (solid)	λ_{abs} [nm]	ε_{max} [$L\,mol^{-1}cm^{-1}$]	λ_{em} [nm]	Φ_{em} [%]
2	yellowish white	402	13900	–	< 0.1
3	pale yellow	440	14800	–	< 0.1
4	yellow	469	18200	484	22
5a	red	534	15600	564	64
5b	red	535	15500	565	63
6	violet	552	17700	582	76
7	blue	620	23300	650	42

[a] The colors are given for the crystalline materials because the coloristic impression for solutions of some of these dyes is influenced by their strong photoluminescence.

Whilst the influence of the core substituent on the absorption properties of these kind of dyes has been reported,[12, 14] the appearance of intense photoluminescence (Figure 2) was a surprise to us because Vollmann's 2,6-arylamino-substituted naphthalene bisimide dyes are nonfluorescent,[13] and hydrogen bonding to carbonyl groups is considered as a major pathway for radiationless deactivation of the excited state that has been applied extensively in the design of UV absorbers.[16] The existence of a strong intramolecular hydrogen bond between the 2- and 6-amino substituents and the proximate carbonyl oxygen atom of **5**–**7** was indeed confirmed by the strongly downfield shifted proton resonance signal of the NH hydrogen atom which appears as a well-defined triplet (owing to the coupling to the neighboring methylene protons) between $\delta = 9.33$ and 10.05 ppm in deuterated chloroform. Nevertheless, despite these arguments dyes **4**–**7** exhibit photoluminescence with quantum yields between 22 and 76% of green (**4**), orange (**5**), and red (**7**) light (Table 1).

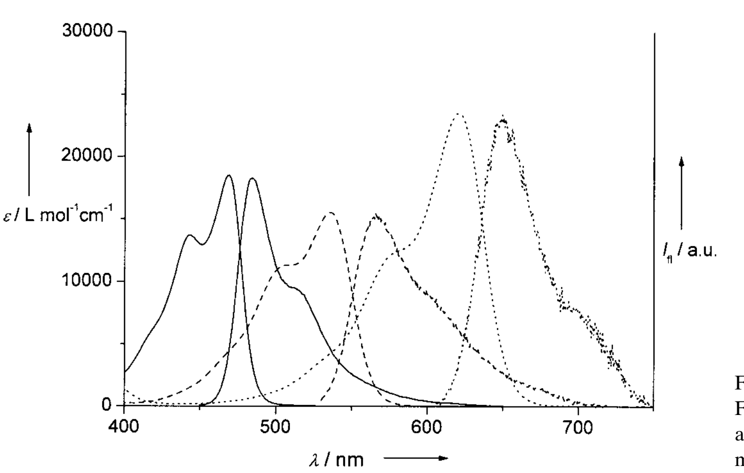


Figure 2. Absorption and fluorescence spectra of dyes **4** (solid line), **6** (dashed line) and **7** (dotted line) in dichloromethane.

Owing to the rather small chromophoric system all dyes **3**–**7** exhibit a very good solubility and do not show any evidence for aggregation even in solvents like methanol or *n*-hexane.[17] Of course in the given case the sterically demanding 2,6-diisopropylphenyl substitutents[18] at the imide-nitrogen atom contribute to prevent aggregation but even with simple *n*-alkyl and other aryl substitutents well-soluble dyes are obtained.[13] For dyes **5a** and **7** the solvatochromic properties were investigated in six solvents of different polarity and a significant bathochromic shift of the absorption as well as emission maxima was noted with increasing solvent polarity (Table 2, Figure 3). For dye **5a** the bathochromic shift from *n*-hexane to methanol amounts to $\Delta\lambda = 11$ nm ($\Delta\tilde{\nu} = 400\ cm^{-1}$) in absorption and to $\Delta\lambda = 52$ nm ($\Delta\tilde{\nu} = 1650\ cm^{-1}$) in emission and for dye **7** the respective values are $\Delta\lambda = 18$ nm ($\Delta\tilde{\nu} = 480\ cm^{-1}$) and $\Delta\lambda = 38$ nm ($\Delta\tilde{\nu} = 930\ cm^{-1}$).

Table 2. Solvent-dependent optical properties of dyes **5a** and **7**.

Solvent	ε_r	λ_{abs} (**5a**) [nm]	λ_{em} (**5a**) [nm]	Φ_{em} (**5a**) [%]	λ_{abs} (**7**) [nm]	λ_{em} (**7**) [nm]	Φ_{em} (**7**) [%]
n-hexane	1.89	521	536	0.51	601	619	0.70
diethyl ether	4.20	525	551	0.58	606	630	0.54
ethyl acetate	6.02	527	565	0.55	609	638	0.48
dichloromethane	8.93	534	568	0.62	621	650	0.41
acetonitrile	35.94	531	580	0.41	615	653	0.33
methanol	32.66	532	588	0.19	619	657	0.31

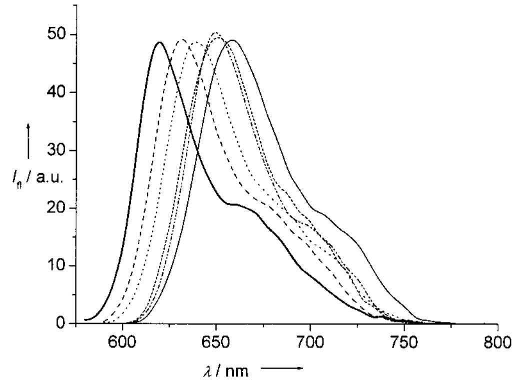


Figure 3. Fluorescence spectra of dye **7** for solvents of increasing polarity. From left to right: (——, thick) *n*-hexane, (- - - -) diethyl ether, (••••) ethyl acetate, (–••–••) dichloromethane, (short dashes) acetonitrile, (——, thin) methanol.

The solvatochromism of the absorption as well as the emission maxima have been evaluated by means of linear free energy relationships (LFER) to the common empirical solvent polarity scales $E_T(30)$ and π^* as well as the Lippert–Mataga equation.[19] All these scales have been shown to be sensitive to the nonspecific (di)polarity of the solvent but exhibit different sensitivities towards additional specific interactions of the solute with the solvent. For example, the $E_T(30)$ scale is strongly influenced by the presence of hydrogen bonding. Thus, it was not too surprising to us that the correlation of the absorption maxima (in wavenumbers $\tilde{\nu}$/ cm^{-1}) was rather good for the apolar and dipolar aprotic solvents hexane, diethyl ether, ethyl acetate, and acetonitrile (whose polarity is mainly governed by the permittivity ε_r) for both dyes **5a** and **7** with the π^* as well as the $E_T(30)$ scale (correlation coefficient >0.95), but dropped significantly if dichloromethane (high contribution of polarizability) and/or methanol (high contribution of hydrogen bonding) were included in the linear regression analysis. In particular for dichloromethane severe deviations from a LFER were observed for the $\tilde{\nu}_{max}$ values of both dyes and the $E_T(30)$ value. In this context it seems especially remarkable that the Stokes shifts, that is the difference between the absorption and emission maxima, for *both* dyes in *all* solvents afforded an excellent correlation to the Lippert–Mataga polarity scale $f(\varepsilon_r,n) = (\varepsilon_r - 1)/(2\varepsilon_r + 1) - (n^2 - 1)/(2n^2 + 1)$ that describes the solvent in a most simplistic dielectric continuum model (correlation coefficient of 0.95 for **5a** and of 0.97 for **7**). In contrast to the other scales this correlation (Figure 4) is not just an empirical LFER but has a physical meaning that relates the positive slope to an increase of the dipole moment $\Delta\mu$ upon optical excitation (positive solvatochromism). However, owing to the molecular symmetry, for dye **7** only changes in the quadrupole moment are feasible which is the most likely reason why a much larger slope is observed for the dipolar dye **5b**.

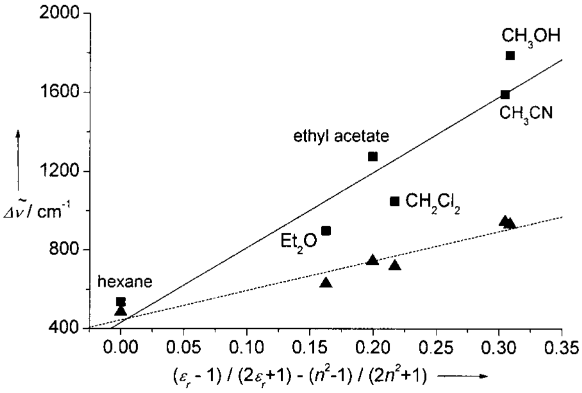
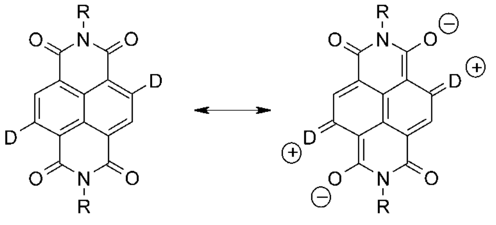


Figure 4. Correlation of the Stokes Shift between the absorption and emission maxima $\Delta\tilde{\nu} = \Delta\tilde{\nu}_{abs} - \Delta\tilde{\nu}_{em}$ and the Lippert–Mataga polarity parameter of the solvent for dyes **5a** (■) and **7** (▲).

The observed absorption properties of these dyes may be explained tentatively based on Scheme 2, which suggests that the electronic S_0–S_1 transition arises from an interaction of the electron-donor substituents with the carbonyl functional groups. If the ground state is dominated by the left unpolar formula and the excited state by the right zwitterionic one we expect positive solvatochromism as observed for all these compounds. To account for the spectral position of the S_0–S_1 transition at rather long wavelength, cross-conjugation between two donor–acceptor systems is assumed to occur as in anthraquinoid and indigoid dyes.[20, 21] For such two-dimensional chromophores a significantly smaller number of double bonds is required to achieve long-wavelength absorbance than in traditional one-dimensional chromophores. For comparison, an extended chain of five conjugated double bonds (leading to thermally and photochemically very unstable dyes) is required to achieve blue color, that is absorption bands above 600 nm, for cyanine and the best conjugated merocyanine dyes.[15, 20] With regard to the fluorescence intensity it seems noteworthy that the quantum yields remain high as long as the solvent has no proton-donating capabilities (Table 2). This points to a radiationless deactivation pathway by means of *intermolecular* hydrogen bonds (in contrast to the *intramolecular* hydrogen bonds discussed above) between the solvent molecules and the carbonyl groups of the dyes. A similar but not as pronounced solvent effect was observed previously for structurally related perylene bisimide dyes.[7b, 22]



Scheme 2. Resonance model for dyes **3**–**7** which explains the strong impact of electron donor substituents D on the absorption and emission wavelengths as well as the significant positive solvatochromism.

To shed more light onto the origin of the color properties of these dyes we analyzed the HOMO and LUMO as well as the transition densities involved in the lowest energy optical transition of *N*,*N*′-dimethylnaphthalene-1,4,5,8-tetracarboxylic acid bisimide and its 2- and 2,6-(bis)dimethylamino-substituted derivatives. These molecular properties were calculated with the CNDO/S method for AM1 optimized geometries and the results are displayed in Figure 5.[23]

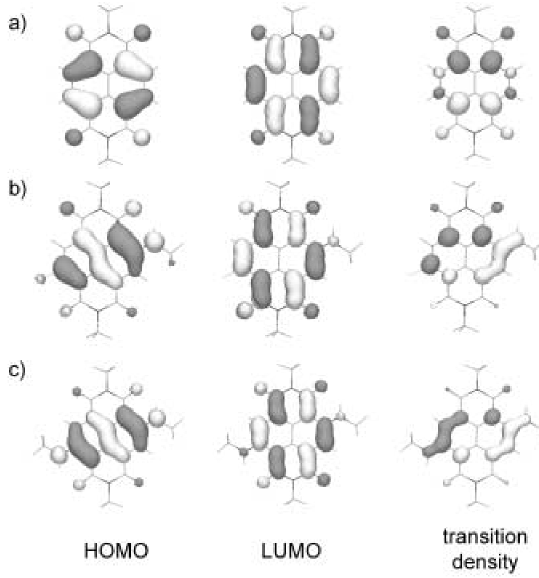


Figure 5. HOMO, LUMO, and transition density for a) *N*,*N*′-dimethyl naphthaline 1,4,5,8-tetracarboxylic acid bisimide and its b) 2-chloro-6-dimethylamino- and c) 2,6-dimethylamino-substituted derivatives according to CNDO/S calculations of AM1 optimized molecules.

The MO calculations reveal a unique change of the transition density for the lowest energy optical transition within the given series of dyes. Thus, whereas the HOMO–LUMO transition of the parent naphthalene bisimide is polarized along the long molecular axis (i.e. between the two imide groups), it is polarized perpendicular to this axis for the 2- and 2,6-substituted derivatives. This feature arises from a 'new' HOMO orbital that is created from the interaction of the electron-donating 2,6-substituents with the naphthalene

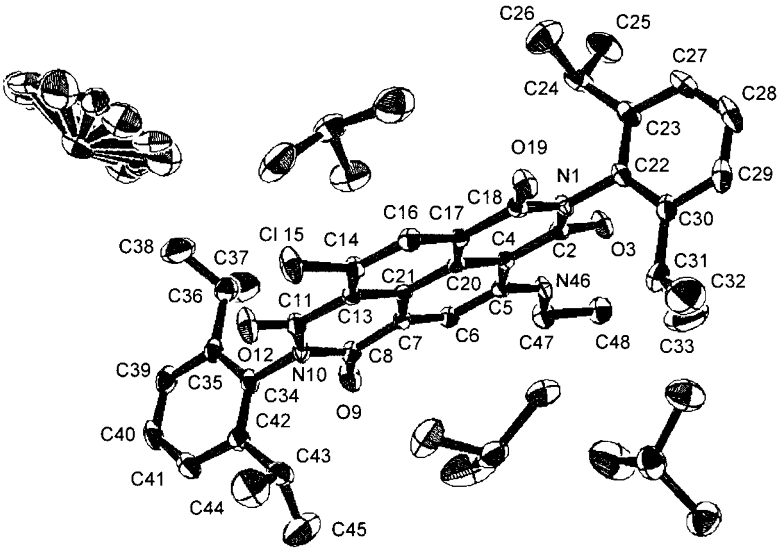


Figure 6. Structure of **5a** (ORTEP plot) in the crystal showing the presence of four molecules of chloroform (one of them disordered) that fill the space created by the orthogonal connection ($\theta = 83°$) of the naphthalene bisimide and the diisopropylphenyl substituents.

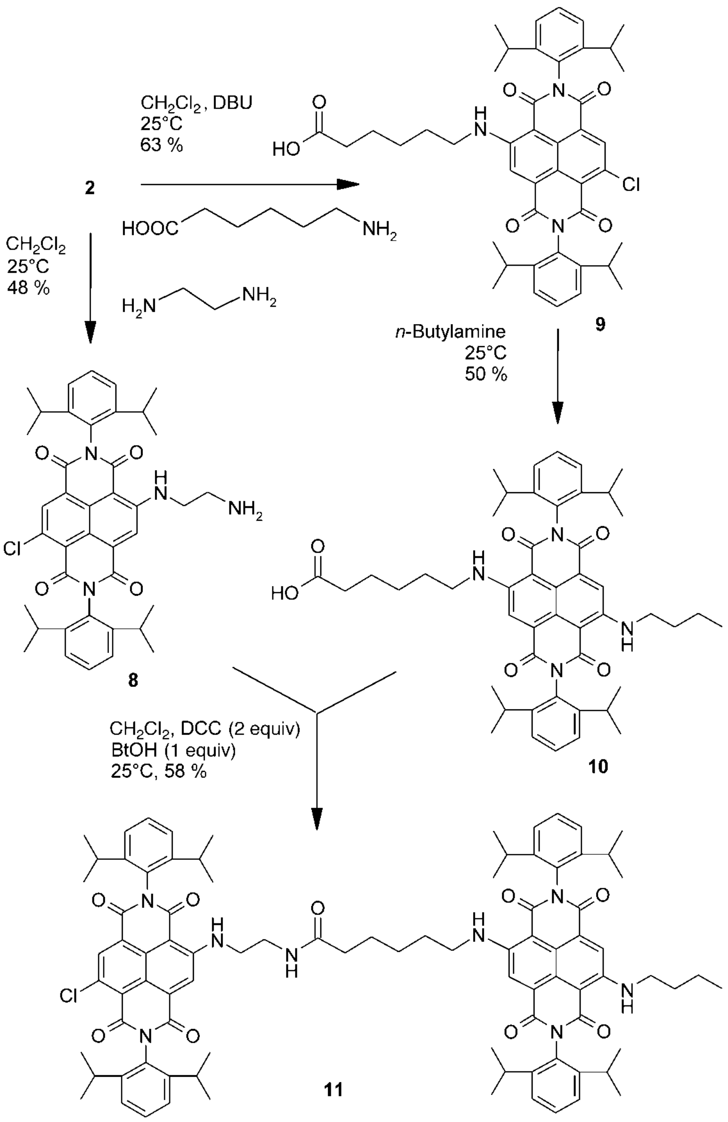
π-conjugated core. On the other hand the LUMO remains unchanged and even the original naphthalene bisimide-typical transition (Figure 5a, right) is also found as a higher energy transition for the 2,6-substituted derivatives. Accordingly the UV/Vis absorption spectra of dyes **3**–**7** (Figure 1) can be explained based on two allowed optical transitions, one at 350 nm that is characteristic for all naphthalene bisimides (Figure 5a; right) and a new long-wavelength charge transfer transition (Figure 5b,c; right) that is polarized perpendicular to the former and whose spectral position is highly dependent on the 2- and 6-electron donor substituents as well as the solvent polarity.

Solid-state properties: Although the 2,6-diisopropylphenyl substituents are not mandatory to prevent aggregation of these dyes in solution[13] they are very supportive for isolating the π systems also in the solid state. As a result the color of all crystals obtained from dyes **3**–**7** essentially reflects the spectral features in solution, and all crystals exhibit intense solid-state photoluminescence. We have succeeded in growing a single crystal of dye **5a** suitable for an X-ray structural analysis (Figure 6) and thus these properties can now be studied in some detail.[18]

The most prominent feature of the structure of **5a** is the perpendicular orientation of the 2,6-diisopropylphenyl groups with respect to the naphthalene bisimide chromophoric unit. This leads to fully isolated chromophores which only experience the surrounding solid or liquid matrix but do not aggregate even in low polarity environments or in the solid state. In the given crystal four molecules of chloroform are intercalated to 'solvate' the dye or—in other words—fill the empty space created by the conformationally restricted dye molecules. All other structural features such as the bond lengths and angles are not unusual. The C–C bond lengths in the planar naphthalene bisimide chromophore are all between 1.36 and 1.48 Å; the longest bonds are found for the connection to the carbonyl groups.

Energy transfer in a bichromophoric model compound: In the last part of this study we demonstrate one possible application of these dyes that might be of interest for FRET (fluorescence resonance energy transfer)[24] studies of biomacromolecules[1] and supramolecular dye assemblies.[8, 9, 25] The usefulness of this class of dyes for such studies became already apparent from Figure 2 where we see a strong overlap of the emission spectrum of dye **4** with the absorption spectrum of dye **6** and a similarly good overlap of the emission spectrum of dye **6** with the absorption spectrum of dye **7**. According to Förster's theory of FRET,[24] long-range through-space resonance energy transfer is expected if such an overlap of the absorption and emission spectra (together with some other features like high fluorescent quantum yields[24]) of the involved chromophores occurs. Thus dyes **3**–**7** constitute a series of dyes that enables the construction of energy transfer cascades[29] based on a single π-conjugated scaffold. As a first example to support this point we synthesized the bichromophoric compound **11** according to Scheme 3 from an amino-substituted derivative of the 'red' dye (**8**) and a carboxy-substituted derivative of the 'blue' dye (**10**) by DCC coupling in the presence of 1-hydroxybenzotriazole (BtOH). For this sequence it was again very helpful that the first chlorine exchange takes place with a much higher reactivity than the second. This enables the isolation and further coupling of **8** as well as the stepwise nucleophilic displacement of the two chlorine atoms of **2** with two different amines to give **10**.

For the bichromophoric compound **11**, absorption, emission, and excitation spectroscopy was carried out in dilute dichloromethane. Based on the structural properties (bulky imide substituents) and the excellent additivity of the absorption bands of the two chromophoric subunits (Figure 7) we can exclude the possibility of *intramolecular aggregation* due to folding of the flexible alkyl spacer. Such aggregation would lead to strong coupling of the two dyes and open alternative through-bond mechanisms of energy transfer.[24b] In addition *intermolecular* FRET processes between different molecules can be ruled out at the applied concentrations of our study because no energy transfer became apparent for equimolar mixtures of dyes **5b** and **7**. In contrast, upon selective illumination of the 'red' dye in the bichromophoric compound **11** at a wavelength of 500 nm we observe a strong emission predominantly from the 'blue' dye (Figure 8) that is now attributed to an *intramolecular* FRET process. From the ratio of the integrated emission bands <600 nm (stemming from the 'red' dye) and >600 nm (stemming from the 'blue' dye) an energy transfer efficiency of about 96% is calculated and a fluorescence quantum yield of 30% com-



Scheme 3. Synthesis of bichromophoric compound **11**.

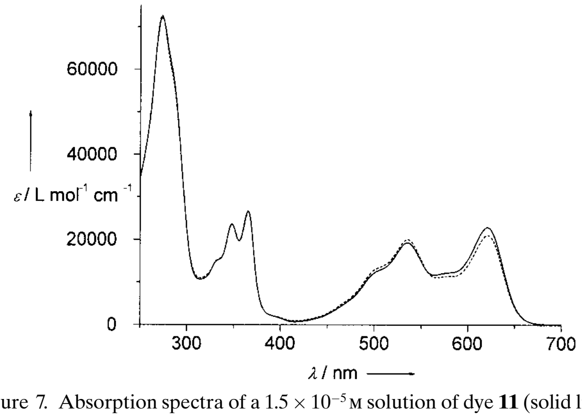


Figure 7. Absorption spectra of a 1.5×10^{-5} M solution of dye **11** (solid line) and of a mixture of dyes **5a** and **7** at the same concentration (dotted line) in dichloromethane.

pared to that of 33% for direct excitation of the 'blue' dye at 622 nm.

Further support for a highly efficient energy transfer process is given by the excitation spectrum in Figure 8 which shows that both absorption bands in the visible as well as the one in the UV can be used to populate the lowest energy excited state of the 'blue' dye in **11**. The slightly reduced intensity of the excitation spectrum for the two bands at 350 and 500 nm (at $\lambda_{em} = 660$ nm) compared to the absorption spectrum is in accord with the additional weak fluorescence from the 'red' dye (at < 600 nm) after excitation of these high energy bands.

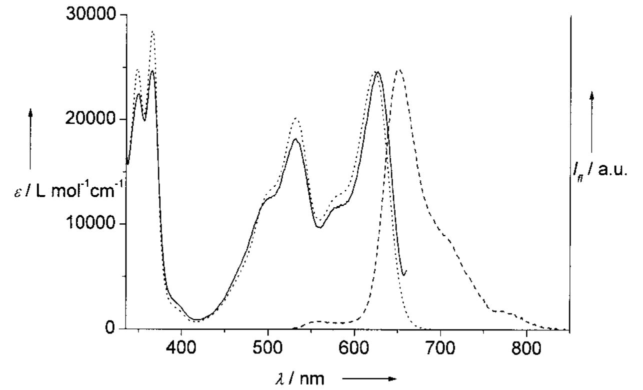


Figure 8. Absorption (dotted line), excitation (solid line; fluorescence detection at 660 nm), and fluorescence (dashed line; excitation at 500 nm) spectra for dye **11** in dichloromethane.

Conclusion

In summary, these studies showed that the introduction of electron-donating alkoxy and alkylamino substituents at the 2,6-positions of naphthalene-1,4,5,8-tetracarboxylic acid bisimides lead to interesting fluorophors. Depending on the respective substituents yellow, red, or even blue dyes are obtained that emit green, orange, or red light with fluorescence quantum yields of up to 76%. If these optical features are combined with the possibility of covalent or supramolecular derivatization at the imide nitrogen atoms we expect a multitude of interesting applications for these dyes.[8–11, 25] One application was already demonstrated that made use of the spectral overlap of the absorption and the emission spectra between two different dyes of the given series of compounds. This allowed us to measure an efficient Förster-type energy transfer (FRET) process within the covalently tethered bichromophoric conjugate **11**. Such photophysical processes are highly desirable for unraveling binding and folding events for biomacromolecules. Therefore it seems noteworthy that the two dyes **8** and **10** are already equipped with useful functional groups for the covalent labeling of oligopeptides and proteins.

Experimental Section

Materials and methods: Solvents and reagents were purchased from Merck (Darmstadt, Germany) unless otherwise stated and purified and dried according to standard procedures.[26]

2,6-Dichloronaphthalene anhydride **1** was obtained as described in reference [12a]. Column chromatography was performed on silica gel (Merck Silica Gel 60, mesh size 0.2–0.5 mm). The solvents for spectroscopic studies were of spectroscopic grade and used as received. UV/Vis spectra were recorded on a Perkin Elmer Lambda 40P spectrometer, and fluorescence spectra were measured on a calibrated Perkin Elmer LS 50B spectrometer in the conventional right-angle set-up in the presence of air for dilute solutions ($A < 0.04$). Fluorescence quantum yields were determined relative to fluorescein ($\phi = 0.9$, 0.1N NaOH)[27a] for dyes **2**–**4** and relative to *N,N'*-di(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide ($\phi = 0.96$, $CHCl_3$)[18a, 27b] for the other dyes. NMR spectra were recorded on a Bruker DRX 400 spectrometer using the proton signal of TMS or the carbon signal of the deuterated solvent as internal standard. Mass spectra were recorded on Varian MAT 711 and Finnigan SSQ 7000 (both EI), Finnigan TSQ 7000 (FAB), and Bruker Franzen Reflex III (MALDI-TOF) spectrometers. The calculated and found *m/z* values correspond to the monoisotopic mass.

X-ray crystal structure analysis of 5a: $C_{40}H_{42}ClN_3O_4 \cdot 4\,CHCl_3$, $M_r = 1141.69$, monoclinic, space group $P2_1/n$ (no. 14), $a = 16.448(5)$, $b = 14.999(5)$, $c = 21.138(5)$ Å, $\beta = 91.765(5)^\circ$, $V = 5212(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.455$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.732$ mm^{-1}, crystal size $0.30 \times 0.23 \times 0.15$ mm, $T = 170$ K, 10117 independent reflections collected, 794 parameters, $R1 = 0.0593$ and $wR2 = 0.1463$ for reflections with $I > 2\sigma(I)$, max./min. residual electron density $0.746/-0.655$ e Å^{-3}. Data were collected using a STOE-IPDS diffractometer with monochromatic (graphite monochromator) $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $2\theta_{max} = 52.040$, $2\theta_{min} = 4.120$); rotation scan modus. The structure was solved by direct methods,[28a] refinement on F^2 using the full-matrix least-squares method.[28b] Hydrogen atoms localized in final difference Fourier map. One molecule of **5a** crystallizes with four molecules of chloroform. One of these chloroform molecules is disordered in the sense that it is rotating around its C–H bond. Four main different positions were located with an occupancy of 50, 30, 15, and 15%. In the final Fourier map two other positions seem also likely but were not taken into account. This explains the high final electron density of 0.746 e Å^{-3} in the map. CCDC-178616 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

***N,N'*-Di-(2',6'-diisopropylphenyl)-2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid bisimide (2):** 2,6-Dichloronaphthalene-1,4,5,8-tetracarboxylic acid bisanhydride **1** (1 g, 2.96 mmol) was suspended in acetic acid (40 mL) and heated at reflux. Into this mixture 2,6-diisopropylaniline (3.75 mL, 20 mmol) was added and the mixture was kept at reflux at 120 °C for another 20 min. The solution was concentrated in vacuo and the remaining residue was poured into methanol (40 mL). The precipitated solid was filtered, dried, and recrystallized from acetic acid to afford a yellowish white solid. Yield: 0.85 g (44%). M.p. 409 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.90$ (s, 2H; H3, H7), 7.51 (t, 2H; H4'), 7.35 (d, 4H; H3',5'), 2.65 (septet, 4H; *i*Pr-H), 1.17 ppm (d, 24H; *i*Pr-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 160.92$, 160.42, 145.28, 140.71, 136.35, 130.00, 129.60, 127.89, 126.15, 124.21, 122.62, 29.29, 23.83 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 402 (13900), 381 (12000), 359 (18900), 251 (51500) nm (L mol^{-1} cm^{-1}); MS (EI, 70 eV): *m/z*: 654 ([*M*]$^+$); elemental analysis calcd (%) for $C_{38}H_{36}Cl_2O_4N_2$ (655.63): C 69.62, H 5.53, N 4.27; found: C 69.65, H 5.58, N 4.34.

***N,N'*-Di-(2',6'-diisopropylphenyl)-2-chloro-6-ethoxynaphthalene-1,4,5,8-tetracarboxylic acid bisimide (3):** To a stirred solution of dichloronaphthalene bisimide **2** (0.325 g, 0.50 mmol) in CH_2Cl_2 (50 mL), sodium ethoxide (136 mg, 2 mmol) was added and stirring was continued for 10 min. Then ethanol (0.5 mL) was added and the reaction mixture was stirred at 25 °C for another 4 h before 1N HCl(10 mL) was added. The organic layer was separated, washed with water (20 mL), and dried over sodium sulfate. Filtration, removal of the solvent, and chromatographic purification on silica with $CHCl_3$ afforded a pale yellow solid. Yield: 0.15 g (46%). M.p. 312 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.84$ (s, 1H; H3), 8.61 (s, 1H; H7), 7.49 (q, 2H; H4'), 7.34 (t, 4H; H3',5'), 4.54 (q, 2H; -OCH_2), 2.68 (septet, 4H; *i*Pr-H), 1.58 (t, 3H; OCH_2CH_3), 1.16 ppm (d, 24H; *i*Pr-CH_3); UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 440 (14800), 418 (10700), 362 (14600), 345 (11600), 212 (40500) nm (L mol^{-1} cm^{-1}); MS (EI, 70 eV) *m/z*: 664 ([*M*]$^+$); elemental analysis calcd (%) for $C_{40}H_{41}N_2ClO_5$ (655.24): C 72.22, H 6.21, N 4.21; found: C 70.48, H 6.30, N 3.96.

***N,N'*-Di-(2',6'-diisopropylphenyl)-2,6-diethoxynaphthalene-1,4,5,8-tetracarboxylic acid bisimide (4):** An ethanolic sodium ethoxide solution was prepared from sodium (46 mg, 2 mmol) and ethanol (1.2 mL). To this solution dichloronaphthalene bisimide **2** (300 mg, 0.45 mmol) was added and the mixture was stirred at 25 °C for 4 h. This solution was poured into 1N HCl (100 mL) and the yellow precipitate was filtered, washed with water, and dried. Purification by chromatography on a silica column with $CHCl_3$ afforded a yellow dye. Yield: 0.16 g (51%). M.p. 347 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.56$ (s, 2H; H3,7), 7.47 (t, 2H; H4'), 7.33 (d, 4H; H3',5'), 4.49 (q, 4H; -OCH_2), 2.71 (septet, 4H; *i*Pr-H), 1.56 (t, 6H; -OCH_2CH_3), 1.17 ppm (d, 24H; *i*Pr-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 162.45$, 160.84, 160.47, 145.44, 130.51, 129.51, 127.43, 124.44, 123.99, 120.50, 111.41, 66.50, 29.12, 23.90, 14.69 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 469 (18200), 443 (13500), 361 (14500), 343(12400), 255 (48000) nm (L mol^{-1} cm^{-1}); fluorescence (CH_2Cl_2), $\lambda_{max} = 484$ nm, quantum yield = 0.22; MS (EI, 70 eV) *m/z*: 674 ([*M*]$^+$); elemental analysis calcd (%) for $C_{42}H_{46}N_2O_6$ (674.84): C 74.75, H 6.87, N 4.15; found: C 73.28, H 6.45, N 4.03.

***N,N'*-Di-(2',6'-diisopropylphenyl)-2-*n*-butylamino-6-chloronaphthalene-1,4,5,8-tetracarboxylic acid bisimide (5b):** To a stirred solution of dichloronaphthalene bisimide **2** (197 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) at 25 °C was added *n*-butylamine (0.5 mL, 5 mmol) and the reaction mixture was stirred at 25 °C for 2 h. It was then poured into 1N HCl (20 mL) and the organic layer was separated, washed with water (20 mL), and dried over sodium sulfate. The solvent was removed and the product was purified by chromatography on silica with $CHCl_3$/*n*-hexane (3:2) to give a red dye. Yield: 85 mg (41%). M.p. 293 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 10.05$ (t, 1H; NH), 8.78(s, 1H; H7), 8.41 (s, 1H; H3), 7.50 (q, 2H; H4'), 7.35(t, 4H; H3',5'), 3.60 (q, 2H; -$NHCH_2$-), 2.68 (septet, 4H; *i*Pr-H), 1.76 (m$_c$, 2H; -NCH_2CH_2-), 1.48 (m$_c$, 2H; CH_2), 1.18 (d, 24H; *i*Pr-CH_3), 0.99 ppm (t, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 166.33$, 162.20, 162.01, 161.28, 152.31, 145.50, 135.57, 133.62, 130.28, 129.83, 129.32, 127.92, 124.20,124.08, 122.53, 122.12, 121.41, 99.90, 43.21, 31.22, 29.32, 29.24, 23.99, 23.89, 20.13, 13.69 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 535 (15500), 503 (11200), 366 (13500), 348(12100), 270 (36600) nm (L mol^{-1} cm^{-1}); fluorescence (CH_2Cl_2): $\lambda_{max} = 565$ nm, quantum yield = 0.63; MS (EI, 70 eV): *m/z*: 691 ([*M*]$^+$); elemental analysis calcd (%) for $C_{42}H_{46}ClN_3O_4$ (692.31): C 72.87, H 6.70, N 6.07; found: C 72.50, H 6.40, N 6.07.

***N,N'*-Di-(2',6'-diisopropylphenyl)-2-ethylamino-6-chloronaphthalene-1,4,5,8-tetracarboxylic acid bisimide (5a):** Dichloronaphthalene bisimide **2** (197 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (30 mL), and ethylamine (70% in water; 1 mL, 20 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, and then poured into 1N HCl (30 mL). The organic layer was separated, washed with water (20 mL), and dried over sodium sulfate. Removal of the solvent and chromatographic separation on silica with $CHCl_3$ afforded a red dye. Yield: 135 mg (68%). M.p. 334 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 9.97$ (t, 1H; NH), 8.77 (s, 1H; H7), 8.39 (s, 1H; H3), 7.50 (q, 2H; H4'), 7.35 (t, 4H; H3',5'), 3.62 (q, 2H; -$NHCH_2$-), 2.67 (septet, 4H; *i*Pr-H), 1.42 (t, 3H; CH_3), 1.17 ppm (d, 24H; *i*Pr-CH_3); UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 534 (15600), 502 (11300), 366(13700), 348 (12300), 270 (39200) nm (L mol^{-1} cm^{-1}); fluorescence (CH_2Cl_2): $\lambda_{max} = 564$ nm, quantum yield = 0.64; MS (EI, 70 eV): *m/z*: 663 ([*M*]$^+$); elemental analysis calcd (%) for $C_{40}H_{42}N_3ClO_4$ (664.25): C 72.33, H 6.37, N 6.33; found: C 71.97, H 6.58, N 6.30.

***N,N'*-Di-(2',6'-diisopropylphenyl)-2-*n*-butylamino-6-ethoxynaphthalene-1,4,5,8-tetracarboxylic acid bisimide (6):** *n*- Butylamine (1 mL, 10 mmol) and 2-chloro-6-ethoxynaphthalene bisimide **3** (100 mg, 0.15 mmol) were stirred at 0 °C for 30 min during which time the color of the reaction mixture changed to red. 1N HCl (25 mL) was added into the stirred mixture to give a pink dye that was filtered, dried, and purified by chromatography on silica with ethyl acetate/*n*-hexane (9:1). Yield: 50 mg (47%). M.p. 317 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 9.79$ (t, 1H; NH), 8.45 (s, 1H; H7), 8.37 (s, 1H; H3), 7.48 (m$_c$, 2H; H4'), 7.34 (m$_c$, 4H; H3',5'), 4.42 (q, 2H; -OCH_2), 3.56 (q, 2H; -$NHCH_2$), 2.71 (septet, 4H; *i*Pr-H), 1.74 (m$_c$, 2H; -$NHCH_2CH_2$-), 1.53 (t, 3H; OCH_2CH_3), 1.47 (m$_c$, 2H; CH_2), 1.17(d, 24H; *i*Pr-CH_3), 0.95 (t, 3H; CH_3); UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 552 (17700), 511 (12200), 369 (12600), 351 (12900), 269 (41000) nm (L mol^{-1} cm^{-1}); fluorescence (CH_2Cl_2): $\lambda_{max} = 582$ nm, quantum yield = 0.76; MS (EI, 70 eV): *m/z*: 701 ([M]$^+$); elemental analysis calcd (%) for $C_{44}H_{51}N_3O_5$ (701.91): C 75.29, H 7.32, N 5.99; found: C 75.26, H 7.62, N 5.67.

***N,N'*-Di-(2',6'-diisopropylphenyl)-2,6-di-*n*-butylaminonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (7):** *n*-Butylamine(1 mL, 10.1 mmol) and dichloronaphthalene bisimide **2** (200 mg, 0.3 mmol) were stirred at 25 °C for 15 min and then refluxed at 85 °C for another 45 min. After cooling to room temperature the mixture was poured into 1N HCl (100 mL) and stirred until a blue precipitate had separated. Filtration and purification by column chromatography with $CHCl_3$/*n*-hexane (1:1) afforded **7** as a blue dye (100 mg (45%)). M.p. 304 °C; ^1H NMR(400 MHz, $CDCl_3$, 25 °C): $\delta =$ 9.33 (t, 2H; NH), 8.26 (s, 2H; H3,7), 7.50 (t, 2H; H4′), 7.35 (d, 4H; H3′,H5′), 3.51(m_c, 4H; $NHCH_2$), 2.70 (septet, 4H; *i*Pr-H), 1.73 (m_c, 4H; CH_2), 1.47 (m_c, 4H; CH_2), 1.17 (d, 24H; *i*Pr-CH_3), 0.94 ppm (t, 3H; CH_3); ^{13}C NMR(100 MHz, $CDCl_3$, 25 °C): $\delta = 160.53$, 163.06, 149.71, 145.61, 130.80, 129.66, 126.30, 124.14, 122.09, 119.18, 101.81, 43.03, 31.28, 29.18, 24.02, 20.23, 13.75 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 620 (23300), 579 (12300), 363(14100), 346 (12000), 281 (41400) nm ($L\,mol^{-1}\,cm^{-1}$); fluorescence (CH_2Cl_2): $\lambda_{max} = 650$ nm, quantum yield = 0.42; MS (EI, 70 eV): *m/z*: 728 ([*M*]$^+$); elemental analysis calcd (%) for $C_{46}H_{56}N_4O_4$ (728.98): C 75.79, N 7.69, H 7.74; found: C 75.68, H 7.54, N 7.74.

***N,N′*-Di-(2′,6′-diisopropylphenyl)-2-(2′-aminoethylamino)-6-chloronaphthalene-1,4,5,8-tetracarboxylic acid bisimide (8):** Naphthalene bisimide **2** (200 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (25 mL) and ethylenediamine (400 mg, 6.66 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. The red colored solution was then poured into 1N HCl (25 mL), the organic layer was separated, and the aqueous layer was extracted twice with CH_2Cl_2 (25 mL). The combined organic extracts were washed twice with water (20 mL) and dried over anhydrous sodium sulfate. Solvent removal and column chromatography on silica with CH_2Cl_2/methanol (98:2) afforded a red dye. Yield: 110 mg, (48%). M.p. 260–65 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 10.21$ (t, 1H; NH), 8.79 (s, 1H; H7), 8.44 (s, 1H; H3), 7.51 (m, 2H; H4’), 7.36 (m, 4H; H3’,5’), 3.67 (m_c, 2H; -$NHCH_2$-), 3.10 (t, 2H; CH_2), 2.68 (m, 4H; *i*Pr-H), 1.39 (bs, 2H; -NH_2), 1.18 ppm (m_c, 24H; *i*Pr-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta =$ 166.33, 162.17, 162.01, 161.25, 152.49, 145.51, 135.63, 133.80, 130.23, 129.84, 129.27, 127.92, 124.18, 122.53, 122.20, 121.43, 100.27, 46.33, 41.15, 29.28, 23.97 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 533 (14800), 366 (13500), 348 (12100), 271 (39000) nm ($L\,mol^{-1}cm^{-1}$); fluorescence (CH_2Cl_2): $\lambda_{max} =$ 570 nm, qunatm yield = 0.53; MS (MALDI-TOF): *m/z*: 679 $[M+H]^+$; HRMS (EI, 70 eV): *m/z*: 678.2966 ([*M*]$^+$); calcd for $C_{40}H_{43}ClO_4N_4$: 678.2972); elemental analysis calcd (%) for $C_{40}H_{43}ClO_4N_4 \cdot 0.8\,CH_2Cl_2$ (747.31): C 65.58, H 6.01, N 7.49; found: C 65.46, H 6.01, N 7.41.

***N,N′*-Di-(2′,6′-diisopropylphenyl)-2-(6-carboxy-*n*-hexylamino)-6-chloronaphthalene-1,4,5,8-tetracarboxylic acid bisimide (9):** Naphthalene bisimide **2** (524 mg, 0.8 mmol) was dissolved in CH_2Cl_2 (50 mL), and 6-aminohexanoic acid (262 mg, 2 mmol) and 1,8-diazobicyclo[5,4,0]-undec-7-ene (DBU) (0.3 mL, 2 mmol) were added. The reaction mixture was stirred at room temperature for 16 h during which time the color of the reaction mixture changed to red. It was then poured into 1N HCl (30 mL), and the precipitate was filtered, dried, and purified by column chromatography on silica with CH_2Cl_2/methanol (98:2) to give a red dye. Yield: 380 mg (63%). M.p. 182 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 10.05$ (t, 1H; NH), 8.78 (s, 1H; H7), 8.39 (s, 1H; H3), 7.50 (m, 2H; H4’), 7.35 (m, 4H; H3′,5′), 3.60 (m_c, 2H; NH-CH_2), 2.66 (m_c, 4H; *i*Pr-H), 2.33 (t, 2H; CH_2), 1.80 (m_c, 2H; CH_2), 1.68 (m_c, 2H; CH_2), 1.50 (m, 2H; CH_2), 1.17 ppm (d, 24H; *i*Pr-CH_3); ^{13}C NMR(100 MHz, $CDCl_3$, 25 °C): $\delta = 175.99$, 163.93, 159.76, 159.54, 158.79, 149.79, 143.03, 133.18, 131.30, 127.77, 127.43, 126.82, 121.73, 121.64, 120.09, 119.69, 118.81, 97.56, 40.74, 31.11, 26.87, 26.79, 26.44, 23.91, 21.69, 21.53, 21.48 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 534 (15000), 500 (10600), 366 (13000), 348 (11700), 332 (8100), 270 (36800), 229 (21100) nm ($L\,mol^{-1}\,cm^{-1}$); fluorescence (CH_2Cl_2): $\lambda_{max} = 568$ nm, quantum yield = 0.61; MS (EI): *m/z*: 749 ([*M*]$^+$); elemental analysis calcd (%) for $C_{44}H_{48}N_3ClO_6$ (750.34): C 70.43, H 6.45, N 5.60; found: C 69.99, H 6.58, N 5.31.

***N,N′*-Di-(2′,6′-diisopropylphenyl)-2-(6-carboxy-*n*-hexylamino)-6-*n*-butylaminonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (10):** Naphthalene bisimide dye **9** (200 mg, 0.26 mmol) was added into an ice-cooled *n*-butylamine solution (1 mL, 10.1 mmol), and the reaction mixture was stirred at room temperature for 16 h during which the color changed to blue. The reaction mixture was then poured into 1N HCl (20 mL) and the precipitate was filtered, dried, and purified by column chromatography on silica with CH_2Cl_2/methanol (98:2). Yield: 105 mg (50%). M.p. 250 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 9.34$ (t, 2H; NH), 8.27 (s, 1H; H3 or H7), 8.24 (s, 1H; H7 or H3), 7.50 (t, 2H; H4’), 7.35 (d, 4H; H3′,5′), 3.50 (m_c, 4H; NH-CH_2), 2.70 (m_c, 4H; *i*Pr-H), 2.32 (t, 2H; CH_2), 1.80–1.64 (m, 6H; CH_2), 1.49 (m_c, 4H; CH_2), 1.17 (d, 24H; *i*Pr-CH_3), 0.94 ppm (t, 3H; CH_3); UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon_{max}) = 620$ (22800), 576 (11800), 363 (13700), 346 (11700), 281 (38700), 227 (35200) nm ($L\,mol^{-1}\,cm^{-1}$); fluorescence (CH_2Cl_2): $\lambda_{max} = 651.5$ nm, quantum yield = 0.40; MS (MALDI-TOF, DHB) *m/z*: 786 ([*M*]$^+$); HRMS (EI, 70eV) m/z: 786.4363 calcd for $C_{48}H_{58}N_4O_6$: 786.4356; elemental analysis calcd (%) for $C_{48}H_{58}N_4O_6 \cdot 0.5\,H_2O$ (796.02): C 72.42, H 7.47, N 7.03; found: C 72.23, H 7.42, N 6.84.

Bichromophoric dye 11: The red amino-substituted dye **8** (40 mg, 0.06 mmol) and the blue carboxy-substituted dye **10** (47 mg, 0.06 mmol) were dissolved in CH_2Cl_2 (25 mL), and 1-hydroxybenzotriazole (8 mg, 0.06 mmol) and dicyclohexylcarbodiimide (25 mg, 0.12 mmol) were added at a temperature of 0 °C under an argon atmosphere. The reaction mixture was allowed to warm up to room temperature and was kept stirring under argon for 24 h. Dicyclohexylurea was removed by filtration and washed with CH_2Cl_2 (20 mL). The combined CH_2Cl_2 solution was evaporated to give a blue solid that was purified by column chromatography on silica with CH_2Cl_2/methanol (99:1). Yield: 50 mg (58%). M.p. 165 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 10.02$ (t, 1H; NH), 9.33 (m_c, 2H; NH), 8.77 (s, 1H; Naph-H), 8.33 (s, 1H; Naph-H), 8.26 (s, 1H; Naph-H), 8.22 (s, 1H; Naph-H), 7.51–7.41 (m_c, 4H; H4′), 7.35–7.31 (m, 8H; H3′,5′), 6.28 (t, 1H; NHCO), 3.53–3.28 (m, 8H; CH_2), 2.70 - 2.61 (m, 8H; *i*Pr-H), 2.13 (t, 2H; CH_2), 1.74–1.67 (m, 6H; CH_2), 1.48–1.41 (m, 4H; CH_2), 1.17–1.13 (m, 48H; *i*Pr-CH_3), 0.94 ppm (t, 3H; CH_3); UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon_{max}) = 622$ (24600), 578 (12700), 531 (20200), 499 (13100), 365 (28500), 348 (21000), 331 (20000), 273 (76900), 228 (55900) nm ($L\,mol^{-1}\,cm^{-1}$); fluorescence (CH_2Cl_2): $\lambda_{max} = 651$ nm; HRMS (FAB, 3-nba): *m/z*: 1447.720 $[M+H]^+$; calcd for $C_{88}H_{100}ClN_8O_9$: 1447.7302; elemental analysis calcd (%) for $C_{88}H_{99}ClN_8O_9 \cdot H_2O$ (1462.28): C 72.28, H 6.96, N 7.66; found: C 71.91, H 6.66, N 7.44.

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