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Photophysical Study of New Versatile Multichromophoric Diads and Triads with BODIPY and Polyphenylene Groups

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The photophysical properties of multichromophoric dyes with borondipyrromethene (BODIPY) and poly-*p*-phenylene (di-*p*-phenylene and tri-*p*-phenylene) groups in the same molecule are studied in detail. The excitation of the polyphenylene moiety in the UV region leads to a strong visible fluorescent emission of the BODIPY chromophore, via intramolecular excitation energy transfer between both groups. Consequently, these multichromophoric dyes are characterized by a large "virtual" Stokes shift, with a high fluorescence capacity and an efficient laser emission. On the other hand, the photophysical properties of a related dichromophoric dye with a hydroxy end group at the di-*p*-phenylene moiety show an important decrease in the fluorescent emission due to a photoinduced electron transfer process in basic media. Therefore, its photophysical properties are sensitive to the environmental acidity/basicity and could be applied as a proton sensor.

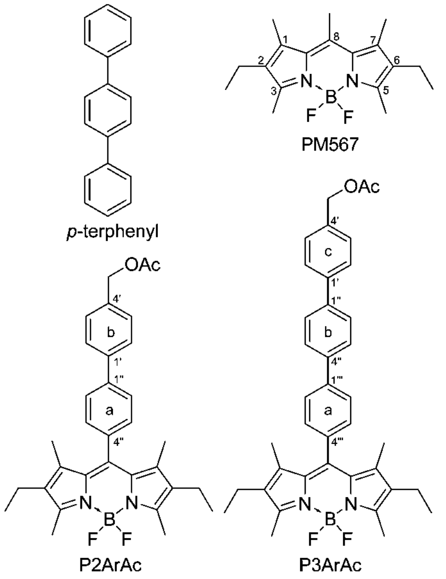
Introduction

In the past few years, borondipyrromethene (BODIPY or BDP) dyes with the core group 4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene have been largely used for many applications in different fields because of their unique photophysical properties.[1−4] As laser dyes, these compounds usually present tunable bands over the spectral region from the visible to the near IR, with high thermostability and high photostability. Their absorption bands are characterized by high absorption coefficients, while the emission bands show high fluorescence quantum yields. This large emission ability, together with their low triplet−triplet absorption, induces high lasing efficiencies.[5,6] Indeed, BDP dyes are becoming the most used active media of tunable dye lasers. Several attempts have been made to develop sintonizable dye lasers in the solid state based on this dye family, improving laser efficiencies and photostabilities.[7,8]

Apart from their applications in photonics, BDP dyes have been widely used as fluorescence probes in biology and biomedicine.[9,10] They have been also applied in analytical chemistry, as molecular sensors to recognize different analytes (cations, anions, or molecules) by means of the fluorescent on/off switch via a photoinduced electron transfer process[11,12] and in optoelectronics (antenna systems),[13−15] in photovoltaic cells, and in digital information storage devices,[16] among others.

The photophysical properties of BDP dyes can be modulated by the incorporation of appropriate substituents to the chromophoric core.[4,6,17] Following this idea, in the last years, the photophysics of a wide variety of BDP analogues with different substituents at central 8 (or *meso)* position, has been analyzed.[6,18,19] Thus, we have incorporated poly-*p*-phenylene (di- or tri-*p*-phenylene) units at this 8-position in the dye PM567, instead of its methyl group, rendering the diads P2ArAc, P3ArAc (both *p*-substituted with a terminal acetoxymethyl group), and P2ArOH (*p*-substituted with an OH), as well as the triad P3ArP (Schemes 1 and 2).

SCHEME 1: Molecular Structures of the Dichromophoric Dyes P2ArAc and P3ArAc and of the Parent Chromophores *p*-Terphenyl and PM567



The dyes P2ArAc and P3ArAc are models of BDP dyes bearing polymerizable end groups, such as the methacryloyloxy group, a good strategy for the covalent linkage of BDP dyes to polymeric chains of, for example, poly(methyl methacrylate), in the design of new tunable dye lasers in the solid state.[20] In addition, the terminal OH group in P2ArOH gives rise to a photophysical behavior sensitive to the OH-ionization and, hence, to the acidity/basicity of the medium. Indeed, some authors have proposed pH fluorescence probes based on the on/off switch of the fluorescence emission of appropriate BDP

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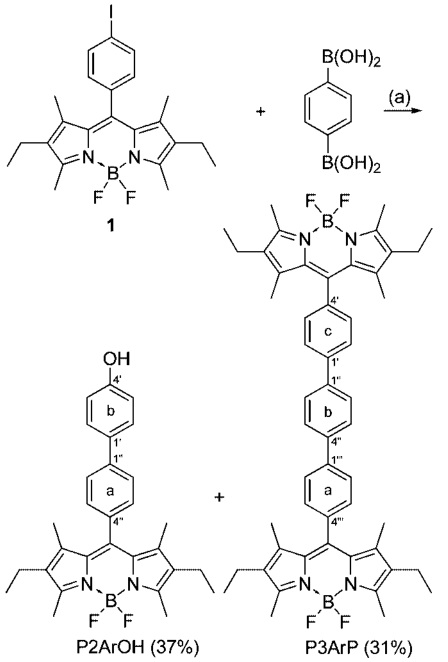
SCHEME 2: Synthesis of the Dyes P3ArP and P2ArOH[a]



[a] Reagents and conditions: (a) $(Ph_3P)_4Pd$, THF-aq; 2 M Na_2CO_3 2:1, reflux, 2 h.

chromophores in acid/basic media due to the activation of quenching processes.[21,22]

The absorption spectrum of some described dichromophoric 8-(poly-*p*-phenylene) BDP dyes is the addition of the individual absorption bands of each chromophore, suggesting the absence of any intramolecular $\pi-\pi$-interaction between both entities in the ground state.[20] Quantum mechanical calculations indicated that both chromophores are disposed nearly perpendicularly, without overlapping their electronic clouds. Excitation at the BDP main absorption band of these dichromophoric dyes leads to the expected emission from the free BDP chromophore, while UV excitation at the poly-*p*-phenylene absorption band induces the same visible fluorescent emission due to the existence of a nonradiative intramolecular excitation energy transfer (intra-EET) from the poly-*p*-phenylene moiety to the BDP group.[20] Some authors have used this intra-EET process for the design of dichromophoric BDP as luminescence traps[23,24] and as excitation energy injectors for the development of light harvesting arrays, antenna systems, or molecular wires.[25−28]

In the present work, the intramolecular excitation energy transfer from di-*p*-phenylene and tri-*p*-phenylene groups linked to a BDP chromophore analogue to that of the dye PM567 (Schemes 1 and 2) is studied. The potential application of the dye P2ArOH, with a terminal phenol group, as acid/base fluorescent sensor is also analyzed, because its fluorescence emission strongly depends on the pH.

Materials and Experimental Methods

Synthesis. The synthesis of the dichromophoric dyes P2ArAc and P3ArAc has been previously reported.[20] The news dyes P2ArOH and P3ArP were synthesized by a Suzuki cross-coupling reaction,[29] as follows (Scheme 2): A mixture of the 8-(*p*-iodophenyl) BDP dye **1**[30] (50 mg, 0.1 mmol), benzene-1,4-diboronic acid (8.2 mg, 0.05 mmol), and tetrakis(triphenylphosphine)palladium(0) (11 mg, 0.01 mmol) in THF-aq; 2 M Na_2CO_3 2:1 v/v (25 mL) was refluxed for 3 h. The reaction mixture was extracted at room temperature with CH_2Cl_2, and the extract was washed with water and dried. Vacuum elimination of the solvent yielded a residue that was separated into two main components by column chromatography on silica gel, with dichloromethane as eluent. Data of 8-(4′-hydroxy-*p*-biphenylene)-4,4-difluoro-2,6-diethyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (P2ArOH): purified by crystallization from hexane at −78 °C; yield, 6.5 mg (27%), red oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.98 (t, J = 7.4 Hz, 6 H, 2 × CH_3CH_2), 1.36 (s, 6 H, CH_3-C1, CH_3-C7), 2.30 (q, J = 7.4 Hz, 4 H, 2 × CH_3CH_2), 2.55 (s, 6 H, CH_3-C3, CH_3-C5), 6.0 (s, 1 H, OH), 6.94 (d, J = 8.4 Hz, 2 H, 2 × H-Ar), 7.30 (d, J = 8.0 Hz, 2 H, 2 × H-Ar), 7.57 (d, J = 8.4 Hz, 2 H, 2 × H-Ar), 7.67 (d, J = 8.0 Hz, 2 H, 2 × H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 10.8 (CH_3), 11.4 (CH_3), 13.6 (CH_3CH_2), 16.0 (CH_3CH_2), 115 (C4′), 127, 128.4, 128.8, 128.9 (CH−Ar), 130.7 (C-7a, C-8a), 132.7 (C-2, C-6), 134.9 (C-1″), 138.3 (C-1, C-7), 139.7 (C-8), 140.1, 140.8 (C-1″, C-4″), 153.8 (C-3, C-5). MS EI (70 eV) m/z (%): 472 [nominal mass, M^+] (100), 457 (99). IR (KBr) ν_{max}: 3150, 1539, 1474, 1314, 1184, 976 cm^{-1}. Data of 4′,4‴-di(4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacen-8-yl)-*p*-terphenyl (P3ArP): purified by crystallization from hexane at −78 °C, red crystals, mp 280 °C. Yield 13 mg (31%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.99 (t, J = 7.4 Hz, 12 H, 4 × CH_3CH_2), 1.38 (s, 12 H, 2 × CH_3-C1, 2 × CH_3-C7), 2.32 (q, J = 7.4 Hz, 8 H, 4 × CH_2CH_3), 2.55 (s, 12 H, 2 × CH_3-C3, 2 × CH_3-C5), 7.38 (m, 4 H, 4 × H-Ar-(b)), 7.80 (m, 8 H, 4 × H-Ar-(a), 4 × H-Ar-(c)) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 11.8 and 12.5 (2 × Ar-CH_3), 14.6 and 17.0 (2 × CH_2CH_3), 127.4 (C-3′,C-5′, C-3‴, C-5‴), 127.5 (C-2′, C-6′, C-2‴, C-6‴), 128.9 (C-2″, C-6″, C-3″, C-5″), 130.7 (C-7a, C-8a), 132.8 (C-2, C-6), 135 (C-4′, C-4‴), 138.3 (C-1, C-7), 139.5 (C-8), 139.8 (C-1″, C-1‴), 140.7 (C-1″, C-4″), 153.8 (C-3, C-5) ppm. MS ESI$^+$ m/z: 815 [M − FH]$^+$. IR (KBr) ν_{max}: 2956, 2920, 2869, 1541, 1476, 1321, 1192, 1074, 978 cm^{-1}. UV−vis (EtOH) λ_{max} (ε): 523 nm (32800 L mol^{-1} cm^{-1}). UV−vis (cyclohexane) λ_{max} (ε): 526 nm (56000 L mol^{-1} cm^{-1}).

Sample Preparation. Solutions of the dyes (ca. 2 × 10^{-6} M) in different media were prepared by adding the corresponding solvent to an adequate amount of a concentrated stock solution (ca. 10^{-3} M) of the corresponding dye in acetone, after vacuum evaporation of the solvent. All the solvents were of spectroscopic grade (Merck and Aldrich) and were used without further purification. Solutions of P2ArOH in ethanol were acidified or alkalinized by adding adequate drops of 7 M HCl in ethanol (prepared by bubbling HCl gas through ethanol up to saturation) or 1 M NaOH in the same solvent, respectively. A special electrode was employed for measuring pH values in ethanol, and a correction factor was used to take into account the effect of this solvent on the value of the proton concentration.

Spectroscopic Techniques. UV−vis absorption and fluorescence spectra were recorded on a Cary 4E spectrophotometer and on a SPEX Fluorolog 3-22 spectrofluorimeter, respectively, with 1-cm quartz cuvettes. Fluorescence spectra were corrected for the monochromator wavelength dependence and the photomultiplier sensibility. Fluorescence quantum yields were determined using as references solutions of PM567 in methanol (Φ = 0.91)[31] (for the BDP Vis emission) and of *p*-terphenyl in cyclohexane (Φ = 0.77)[32] (for the poly-*p*-phenylene UV emission).

Radiative decay curves were registered with the time-correlated single-photon counting technique (Edinburgh Instruments, model FL920, with picosecond time-resolution). Emission was monitored at the maximum emission wavelength after

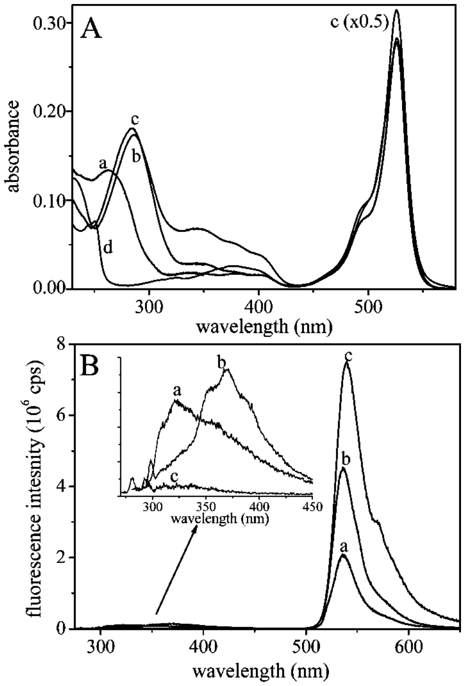


Figure 1. Absorption (A) and fluorescence (B) (UV excitation) spectra of diluted solutions of P2ArAc (a), P3ArAc (b), P3ArP (c), and PM567 (d) in cyclohexane. For a better comparison, the visible absorption band of P3ArP is shown divided by two.

excitation at 410 nm by means of a diode laser (PicoQuant, model LDH410) with 150 ps fwhm pulses, 10 MHz repetition rate, and a power supply of 0.65 mW. The fluorescence lifetime (τ) was obtained from the slope after the deconvolution of the instrumental response, obtained by means of a Ludox scatter solution. The goodness of the deconvolution was controlled with the chi-square (χ^2) and Durbin−Watson (DW) parameters and with the analysis of the residuals. The decay curves were also registered at different excitation and emission wavelengths, in this case by means of a single-photon counting instrument with a nanosecond time resolution (Edinburgh Instruments model ηF900), and exciting with a hydrogen flash-lamp with 1.5 ns FWMH pulses and 40 kHz repetition rate.

Theoretical Methods. Quantum mechanical calculations were performed with the Gaussian 03 software.[33] Ground state geometry was optimized by the B3LYP method using the double valence 6-31G basis set. The absorption and fluorescence Franck−Condon transition was predicted by the time dependent (TD-B3LYP) method. The effect of ethanol in all the above properties was simulated by means of the polarizable continuum model (PCM).

Results and Discussion

Intramolecular Energy Transfer. The absorption and fluorescence spectra of the multichromophoric dyes P2ArAc, P3ArAc, and P3ArP are shown in Figure 1. Similar results were observed for P2ArOH, an analogue of P2ArAc with a *p*-OH group instead the *p*-acetoxymethyl group. The absorption spectrum of all these dyes consists of a UV band (not observed in the dye PM567) and the expected visible absorption band of the BDP group (Figure 1A). The UV absorption band is attributed to the 8-(poly-*p*-phenylene) substituent and, consequently, the absorption spectrum of these multichromophoric dyes can be explained as the addition of the absorption bands of the individual chromophores.

UV excitation leads to a weak fluorescence emission of the corresponding poly-*p*-phenylene unit in the UV, and to the typical strong visible fluorescent band of the BDP group (Figure 1B). The model dye PM567 does not show any important fluorescent emission upon UV excitation. These results indicate the existence of an intra-EET process from the donor poly-*p*-phenylene to the acceptor BDP group. Indeed, the fluorescence emission of the poly-*p*-phenylene chromophore is strongly quenched ($\Phi < 0.02$), favoring the visible emission from the BDP chromophore. This emission is far away from the UV excitation, leading to a very large “pseudo” Stokes shift (ca. 17700 cm^{-1}). This is a very attractive feature for laser dyes and fluorescent labels and probes, since scattering interferences of the pumping/excitation light are neglectable at the emission detection region.[34]

The absorption spectrum of the trichromophoric dye P3ArP (Figure 1A, curve c) does not show any new absorption band, and the shape resembles that of P3ArAc (Figure 1A, curve b). These experimental data suggest the absence of intramolecular interaction between the two BDP groups in P3ArP. This could be due to the length and rigidity of the tri-*p*-phenylene group, avoiding a possible overlapping between the electronic π-systems of the BDP moieties. However, intramolecular BDP−BDP interactions have been reported by some authors when both chromophoric groups are linked through appropriate flexible chains.[35] The intra-EET process between BDP and tri-*p*-phenylene groups is very efficient, since almost no emission is detected from the tri-*p*-phenylene chromophore under UV excitation, and only the typical bright emission of the BDP group is observed (Figure 1B, curve c). The efficient intra-EET process is attributed to the presence of two acceptor units connected at both sides of the donor tri-*p*-phenylene moiety.

The photophysical properties of P3ArP are shown in Table 1. In general, the spectral properties are similar to those of P2ArAc and P3ArAc.[20] The most remarkable feature is the high molar absorption coefficient, which is nearly twice that of the dyes with a single BDP group, indicating that the absorption transition of each BDP chromophore is additive.[36] Indeed, quantum mechanical calculations reveal that the S_0−S_1 absorption band of P3ArP corresponds to promotion of an electron from the HOMO to the LUMO + 1 state and from the HOMO − 1 to the LUMO of the whole molecule. Looking to these molecular orbitals (Figure 2), the HOMO and LUMO + 1 states actually represent the HOMO and LUMO states of one of the two BDP units, and the HOMO − 1 and LUMO states of P3ArP correspond to the HOMO and LUMO states of the second BDP unit. Therefore, the S_0−S_1 absorption band of P3ArP is the electronic transition of two independent HOMO−LUMO BDP transitions. This theoretical result corroborates experimental data in the sense that there is not any delocalization of the excitation energy between both BDP groups and that the absorption is additive, about twice the transition probability in the model dye PM567.

To study the dynamics of the intra-EET, time-resolved fluorescence decay curves at different excitation and emission wavelengths were registered. Figure 3 shows illustrative decay curves for the specific case of P3ArAc. The fluorescent decays of the free related chromophores *p*-terphenyl and PM567 are well-described by a monoexponential analysis, with corresponding lifetimes of around 1 and 6 ns. The fluorescent decay of the BDP chromophore in P3ArAc, after excitation at 490 nm, was also analyzed ($\lambda_{\mathrm{fl}} = 535$ nm) as a monoexponential decay, although the obtained lifetime (4.8 ns) is lower than that of the parent dye PM567 (6.1 ns).[31] This decrease of the fluorescence

TABLE 1: Photophysical Properties of the Dye P3ArP under Visible Excitation in Six Representative Solvents[a]

dye	solvent	λ_{ab} (±0.2 nm)	ε_{max} (±0.5 10^4 mol^{-1} l cm^{-1})	λ_{fl} (±0.2 nm)	Φ (±0.05)	τ (±0.1 ns)	k_{fl} (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
P3ArP	F3-ethanol[b]	521.4	10.4	536.5	0.63	6.4	0.98	0.58
	methanol	522.2	9.6	536.9	0.57	4.9	1.15	0.87
	ethanol	522.8	11.4	537.8	0.54	5.0	1.08	0.92
	acetone	522.0	14.4	537.7	0.50	4.5	1.11	1.11
	ethyl acetate	522.4	14.7	537.9	0.55	4.9	1.13	0.93
	c-hexane	526.0	13.0	540.6	0.45	3.6	1.25	1.52
P2ArAc	c-hexane	526.2	7.0	538.0	0.51	3.4	1.49	1.43
P3ArAc	c-hexane	525.8	7.0	536.9	0.51	3.5	1.46	1.40

[a] Absorption (λ_{ab}) and fluorescence (λ_{fl}) wavelengths, molar absorption coefficient (ε_{max}), fluorescence quantum yield (Φ), and lifetime (τ), radiative (k_{fl}) and nonradiative (k_{nr}) rate constants. The corresponding data of P2ArAc and P3ArAc in cyclohexane (c-hexane) are included for comparison.[20] [b] F3-ethanol = 2,2,2-trifluoroethanol

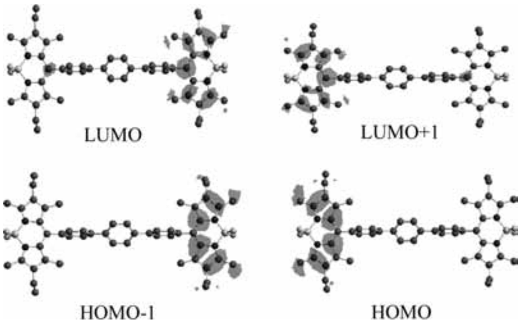


Figure 2. Contour maps of the molecular orbitals HOMO − 1, HOMO, LUMO, and LUMO + 1 of P3ArP, calculated by the AM1 method.

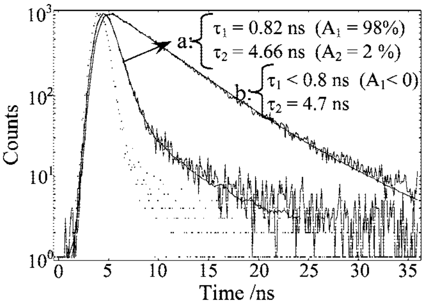


Figure 3. Fluorescence decay curves of P3ArAc in methanol exciting at 275 nm and monitoring the emission at 370 (a) and 535 nm (b).

lifetime, previously observed in a related dye with the 8-(*p*-acetoxymethyl)phenyl group (5.2 ns),[37] has been assigned to an enhancement in the nonradiative deactivation rate constant due to the presence of the phenyl group.[37]

The fluorescence decay of the tri-*p*-phenylene moiety in P3ArAc after UV excitation (λ_{exc} = 275 nm, λ_{fl} = 370 nm) becomes biexponential (Figure 3, curve a), with a main component (98%) with a lifetime lower than that of the free *p*-terphenyl unit (<1 ns, below the time-resolution of the ns SPC instrument), and a minor component (2%) with a longer lifetime (4.6 ns). The fluorescent visible decay of the BDP chromophore in P3ArAc after UV excitation in the tri-*p*-phenylene group (λ_{exc} = 275 nm, λ_{fl} = 535 nm) was analyzed with a grown-in component (with a very short lifetime, lower than the time-resolution of our ns SPC) and a decay component with a fluorescence lifetime of 4.75 ns (Figure 3, curve b), suggesting that in this case the maximum population of the fluorescent excited-state is not reached just after the excitation pulse, but rather after the short delay time required for the transference of the excitation energy from the tri-*p*-phenylene group to the BDP chromophore. The intramolecular energy transfer process decreases the lifetime of the tri-*p*-phenylene group to a value lower than 0.8 ns (the time resolution of the flash-lamp SPC instrument). The lifetime of the BDP chromophore (ca. 4.6 ns) affects the fluorescence decay of the tri-*p*-phenylene moiety when recorded in the experimental conditions in which no emission from the BDP group was observed: λ_{exc} = 275 nm and λ_{fl} = 370 nm.

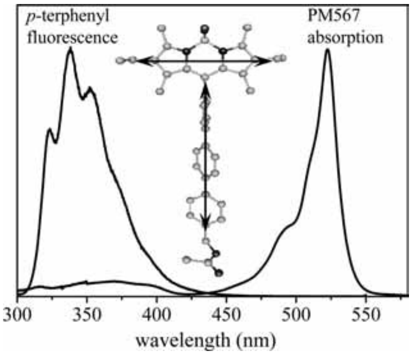


Figure 4. Spectral overlap of the *p*-terphenyl emission band and the PM567 absorption spectrum. Inset: transition dipole moment orientation of both entities in the dichromophoric dye P3ArAc.

Intra-EET mechanisms have been explained by two main theories: the dipole−dipole coupling, or long-range energy transfer, described by Förster[38,39] and the exchange interaction, or short-range energy transfer, formulated by Dexter.[40] In the present case, the studied multichromophoric dyes do not appropriately fulfill some of the requirements needed for the Föster mechanism. For instance, Figure 4 shows that the spectral overlap between the normalized fluorescence band of the donor tri-*p*-phenylene group and the absorption spectrum of the acceptor BDP chromophore (PM567) is nearly neglectable. Moreover, quantum mechanical calculations predict that the transition dipole moment of each chromophore is polarized along the longer molecular axis, leading to a perpendicular disposition of both dipoles in P3ArAc (Figure 4), for which the Föster formalism avoids any energy transfer process. On the other hand, the exchange interaction mechanism for energy transfer implies overlap between the electronic clouds of the involved partners, which is not the case for P3ArAc, where the electronic π-systems of both moieties are disposed nearly perpendicular (Figure 4), as discussed above.

An alternative mechanism for the intramolecular energy transfer consists of the transfer of excitation energy from the donor to the acceptor through the chemical bonds linking both moieties.[41−44] This mechanism does not require a spectral overlap, but demands an orbital interaction, which can take place over a large distance via a conjugated linking chain (superexchange).[45] Moreover, some authors have reported efficient intra-EET in rigid systems in which the donor and the acceptor are separated far away by rigid nonconjugated linkers.[41−43]

Quantum mechanical calculations suggest that the UV absorption of *p*-terphenyl and the visible fluorescence band of

SCHEME 3: (Left) Intramolecular Energy Transfer Mechanism in the Dyes P2ArAc and P3ArAc; (right) Electronic Density of *p*-Terphenyl and PM567 in the HOMO and LUMO States

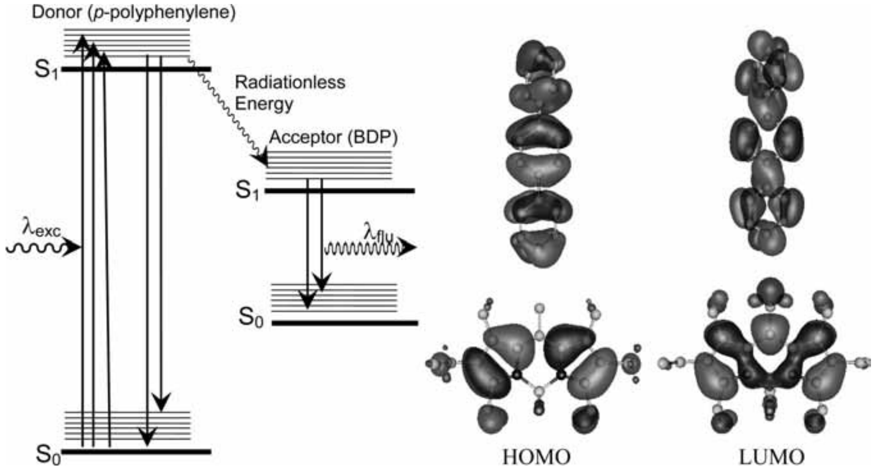


TABLE 2: Photophysical Properties of PAr2OH in Diluted Solution (2×10^{-6} M) of Several Solvents

	c-hexane	acetone	ethanol	methanol
λ_{ab} (±0.2 nm)	525.5	522.0	523.0	522.0
ε_{max} (±0.5 10^4 mol^{-1} l cm^{-1})	4.1	4.0	4.7	3.9
λ_{fl} (±0.2 nm)	538.0	535.5	536.5	535.5
Φ (±0.05)	0.53	0.59	0.60	0.65
τ (±0.1 ns)	3.6	4.5	5.1	4.8
k_{fl} (10^8 s^{-1})	1.46	1.32	1.18	1.35
k_{nr} (10^8 s^{-1})	1.30	0.92	0.79	0.72
$\Delta\nu_{St}$ (cm^{-1})	440	480	495	490

the model dye PM567 are due to the S_1-S_0 transition between the corresponding HOMO and LUMO states of the respective chromophores. The corresponding contour maps for each dye are depicted in the right side of Scheme 3. When these chromophores are linked through the 8-position of the BDP, as in P3ArAc, an important orbital interaction was observed between both chromophores at the linking position in the LUMO state. This observation supports the validity of the through-bond mechanism for the intra-EET process from the excited-state of the tri-*p*-phenylene group to the BDP chromophore (left side of Scheme 3). Such through-bond mechanism has been also proposed for the intra-EET in anthracene-BDP or porphyrin-BDP systems,[14,27] which mainly depends on the nature of both π-systems.[24] In any case, small contributions of the Föster long-distance EET cannot be excluded because of the weak overlapping between the fluorescence band of the tri-*p*-phenylene group and the S_0-S_2 absorption band of the BDP chromophore, as has been proposed for several 8-pyrenyl substituted BDPs.[46,47] Indeed, the preexponential ratio for the fluorescence decay curves of P3ArAc, analyzed at the visible BDP emission after excitation at the UV tri-*p*-phenylene moiety, did not reach the -1 value expected for a complete population of the fluorescent excited-state from the locally excited-state of the tri-*p*-phenylene group, suggesting a partial direct excitation of the BDP chromophore in the UV excitation (i.e., via S_0-S_2 excitation and consecutive ultrafast internal conversion to the fluorescent S_1 state).

Proton Sensor. The dye P2ArOH is also obtained in the synthesis of P3ArP (Scheme 1). Table 2 summarizes its photophysical properties under direct excitation of the BDP group. The spectral properties of P2ArOH are very similar to those of P2ArAc,[20] and the former dye also shows the above commented intra-EET process under UV excitation. However, these two dyes differ in their photophysical behavior in acid/basic media, because the behavior of P2ArOH strongly depends on the ionization of its phenol group and, hence, on the OH^- concentration.

The absorption spectra of P2ArOH in ethanol remain nearly unaltered in media with pH values in the range 0−13.1 (data not shown). However, the fluorescence intensity shows a drastic decrease in basic media (Figure 5). The fluorescence quantum yield slight decreases from $\Phi = 0.60$ in very acid media ($[H^+] = 1$ M) to 0.56 at moderate basic media (pH = 9.2). Further pH increases imply a strong decrease in the fluorescence quantum yield Φ, reaching a value of less than 0.07 at pH = 13.1 (Figure 5B). The proton association constant (K_a) value

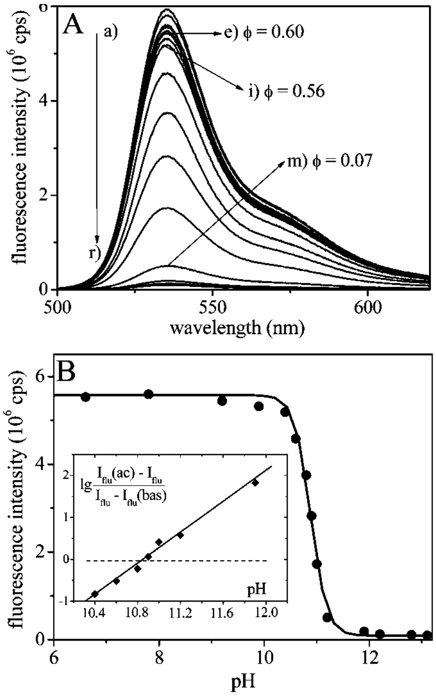
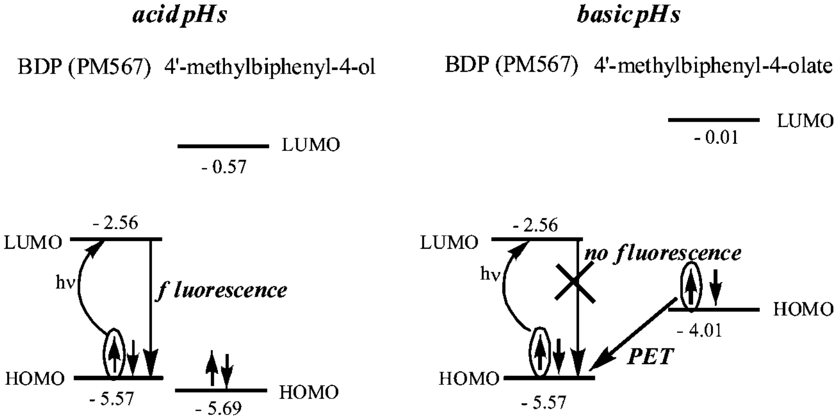


Figure 5. (A) Fluorescence spectra of diluted ethanol solutions of P2ArOH at different pH values: (a) 0, (b) 0.9, (c) 2.8, (d) 5.2, (e) 6.6, (f) 7.8, (g) 9.2, (h) 9.9, (i) 10.4, (j) 10.6, (k) 10.8, (l) 10.9, 9m) 11.0, (n) 11.2, (o) 11.9, (p) 12.2, (q) 12.9, (r) 13.1. (B) Plot of the fluorescence intensity at the maximum wavelength versus the solvent pH. Inset: linear fit of eq 1 (see text).

SCHEME 4: Energy (in eV) of the Frontier Orbitals in Ethanol of PM567 and of Biphenyl-4-ol in Its Neutral -ol (acid pHs) and Ionized -olate (basic pHs) Forms, calculated by the B3LYP Method



can be evaluated for the phenol OH group by the linear relationship of Henderson−Hasselbach (eq 1):

$$\log\frac{I_{\mathrm{fl}}(\mathrm{ac}) - I_{\mathrm{fl}}(\mathrm{pH})}{I_{\mathrm{fl}}(\mathrm{pH}) - I_{\mathrm{fl}}(\mathrm{bas})} = \mathrm{pH} + \log K_{\mathrm{a}} \qquad (1)$$

from which an association constant $K_a = 1.6 \times 10^{-11}$ is deduced (inset Figure 5B, correlation coefficient $r = 0.989$). This value is quite similar to that reported for 4-phenyl-phenol ($K_a = 1.4 \times 10^{-11}$ in water/ethanol mixture[48]). The association constant in the S_1 excited state (K_a*), estimated from the fluorescence wavenumber shift of the acid and basic forms, and the Förster cycle is 2.5×10^{-11}, a value similar to that obtained in the ground state.

The decay curves of P2ArOH (data not shown) are well analyzed as monoexponentials with a lifetime of ca. 5.05 ns in the pH range 0−10.8. In more basic environments the fluorescent decay becomes biexponential, with a major component (98%) with a lifetime of 4.8 ns, and a minor one (2%) with a shorter lifetime (0.7 ns). Moreover, the fluorescence quenching in basic media is reversible, since the bright emission of the BDP group is recovered after acidification. These results suggest that P2ArOH can be applied as a reversible fluorescent on/off switch, since it is highly fluorescent in acid-neutral media and nearly nonfluorescent in basic media.

For a deeper interpretation of the influence of the acidity on the photophysics of P2ArOH, the energy levels of the frontier HOMO and LUMO orbitals of BDP (PM567) and 4′-methylbiphenyl-4-ol in its neutral -ol and ionized -olate forms, moieties are illustrated in Scheme 4. Unfortunately to our knowledge, the ionization potential and electronic affinity of the compounds have not been published. For this reason, the energy values included in Scheme 4 are obtained from quantum mechanical calculations in which the effect of ethanol as solvent is taken into account. The validity of these quantum mechanical data have been previously proven.[8,9]

In acid media (neutral -ol form), the HOMO and LUMO orbitals of 4′-methylbiphenyl-4-ol are placed at lower and higher energies, respectively, with respect to the corresponding HOMO and LUMO states of the BDP chromophore (left side of Scheme 4). Such a disposition of the energy levels suggests that the presence of diphenyl-4-ol does not affect the fluorescent emission of the BDP chromophore. However, in highly basic media the OH group is ionized and the energy of the HOMO and LUMO frontier orbitals of the resulting -olate form of biphenyl-4-ol partner increases in such a way that the HOMO orbital is placed between the HOMO and LUMO levels of the BDP chromophore (right side of Scheme 4). Consequently, when the BDP core is excited, an electron from the HOMO state of the ionized phenol can be transferred (a thermodynamically favored process) to the HOMO state of the BDP, filling the semivacant HOMO orbital and avoiding the radiative transition of the excited electron back to the ground state.

Therefore, quantum mechanical calculations suggest that the loss of the fluorescent emission of P2ArOH in basic media could be assigned to a photoinduced electron transfer (PET) process from the HOMO state of the ionized phenol group to the semivacant HOMO state of excited BDP group in the same molecule. Unfortunately the oxidation potential of the donor moiety 4′-methylbiphenyl-4-olate has not been reported in the literature and, consequently, the Rehn−Weller equation cannot be applied to calculate the free Gibbs energy change of the PET process. The PET process is experimentally confirmed by fluorescence decay curves (data not shown). The PET process should be very rapid, probably in a few picoseconds time-scale, much faster than the time resolution of our ps SPC instrument (around 30 ps), and the corresponding rate constant cannot be evaluated in the present paper. Moreover, quantum mechanical data included in Scheme 4 confirm the viability of PET from the HOMO level of the biphenyl-4-olate moiety to the semivacant HOMO state of PM567 after excitation removing any emission from the excited-state of PM567. The validity of the quantum mechanical data is supported by the fact that the reported reduction potential of PM567 in acetonitrile (−1.29 eV[49]) is very similar to that calculated from the quantum mechanics methods used in the present paper (−1.35 eV).

Summarizing, P2ArOH is a versatile fluorescent dye that shows a large Stokes shift under UV excitation at the di-*p*-phenylene group, and the bright fluorescent emission generated from the BDP chromophore comes from an efficient intra-EET process. This dye can also be used as a proton sensor due to the reversible dependence of its fluorescence emission with the acidity/basicity of the medium.

Conclusions

To find new photophysical processes and to extend the potential applications of BDP laser dyes, an appropriate methodology is to incorporate different chromophores to their structures, for example at the central 8-position, to reach multichromophoric systems. Poly-*p*-phenylene-BDP dyes herein studied present an intramolecular energy transfer process from the donor polyphenylene unit (excitation in the UV) to the acceptor BDP group (emission in the visible), mainly via a through-bond mechanism, with an important "pseudo" Stokes shift which reduces the effects of reabsorption and reemission phenomena. Besides, these dyes convert the UV light into yellow luminescence and, hence, can be used as antenna systems in photovoltaic solar cells or, simply, to achieve light of different wavelengths.

The dichromophoric dye P2ArOH is even a more versatile system since, apart from its large "pseudo" Stokes shift, the presence of the terminal OH-phenyl group induces fluorescence properties sensitive to the acid/basic characteristics of the surrounding environment. In basic media, the phenol OH group is ionized and, after excitation of the BDP moiety, a photoinduced electron transfer process is activated, quenching the BDP fluorescent emission. Thus, P2ArOH dye behaves as a proton sensor with a reversible on/off switch of its visible fluorescence.

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