

Push-Pull Fluorophores Based on Imidazole-4,5-dicarbonitrile: A Comparison of Spectral Properties in Solution and Polymer Matrices

Martin Danko · Pavol Hrdlovič · Jiří Kulhánek · Filip Bureš

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Abstract Spectral properties of novel type of fluorophores consist of a π -conjugated system end-capped with an electron-donating *N,N*-dimethylaminophenyl group and an electron-withdrawing imidazole-4,5-dicarbonitrile moiety were examined. An additional π -linker separating these two structural units comprises simple bond (B1P), phenyl (B2B), styryl (B3S) and ethynylphenyl (B4A) moieties. The absorption and fluorescence spectra were taken in cyclohexane, chloroform, acetonitrile, methanol and in polymer matrices such as polystyrene, poly(methyl methacrylate) and poly(vinylchloride). The longest-wavelength absorption band was observed in the range of 300 to 400 nm. Intense fluorescence with quantum yields of 0.2 to 1.0 was observed in cyclohexane, chloroform and in polymer matrices within the range of 380 to 500 nm. The fluorescence was strongly quenched in neat acetonitrile and methanol. The fluorescence lifetimes are in the range of 1–4 ns for all measured fluorophores. The large Stokes shift (4,000 to 8,000 cm^{-1}) indicates a large difference in the spatial arrangement of the chromophore in the absorbing and

the emitting states. The observed fluorescence of all fluorophores in chloroform was quenched by 1-oxo-2,2,6,6-tetramethyl-4-hydroxy piperidine by the diffusion-controlled bimolecular rate (cca $2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$). Polar solvents such as acetonitrile and methanol quenched the fluorescence as well but probably via a different mechanism.

Keywords Fluorescence · Push-pull · Imidazol-3,4-dicarbonitrile · Polymer matrices

Introduction

The push-pull systems end-capped with strong donors (D) and acceptors (A) connected by π -conjugated paths with various lengths and structures exhibit interesting optical and spectral properties due to intramolecular charge transfer (ICT) [1]. Substituted stilbenes or malondinitrile/benzaldehyde-based compounds are typical representatives of this class of chromophores. A typical arrangement of these chromophores is a D- π -A system with strong electron-donating groups ($-\text{NH}_2$, $-\text{NR}_2$ or $-\text{OR}$) as D and strong electron-withdrawing groups ($-\text{NO}_2$ or $-\text{CN}$ group) as A. These molecules exhibit various degrees of flexibility in the ground and excited state that might be correlated with the relevant radiation and radiationless processes. The spectral properties of the compounds featuring ICT attract considerable attention both in photochemistry and photobiology because of their high susceptibility to some environmental parameters, such as micro-viscosity and micro-polarity [1–7].

During the last three decades, these readily polarizable systems were intensively studied as promising materials for non-linear optics (NLO) [8], optical data storage devices [9], organic light emitting diodes (OLED) [10], organic-inorganic hybrid materials [11], functional polymers [12]

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M. Danko (✉) · P. Hrdlovič
Department of Photochemistry of Polymers Slovak Academy of Sciences, Polymer Institute, Center of Excellence GLYCOMED, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
e-mail: upoldan@savba.sk

J. Kulhánek · F. Bureš
Institute of Organic Chemistry and Technology,
Faculty of Chemical Technology, University of Pardubice,
Študentská 537,
53210 Pardubice, Czech Republic

and dendrimers [13, 14]. More recently, we have reported on new push-pull systems featuring imidazole as the main π -conjugated backbone [15–17]. In the latter two cases [16, 17], imidazole-4,5-dicarbonitrile moieties were used as the electron-withdrawing units. The desired D- π -A push-pull systems were gained by attaching the strong electron-donating *N,N*-dimethylaminophenyl moiety via systematically extended π -conjugated linkers [16]. In the present paper, we report some spectral characteristics of four novel push-pull systems featuring 1-methylimidazole-4,5-dicarbonitrile and *N,N*-dimethylaminophenyl units linked with additional π -linkers, such as single bond (B1P), phenyl (B2B), styryl (B3S) and ethynylphenyl (B4A) moieties. The main goal of this paper is to characterize these new fluorophores exhibiting intramolecular charge transfer (ICT) in various liquid media as well as in solid polymer matrices with respect to their potential practical application in photonics.

Experimental

The molecular structures of the investigated fluorophores B1P, B2B, B3S and B4A are given in Scheme 1. Their detailed synthesis was published elsewhere [16].

Anthracene was zone refined (Aldrich) purity and was used as received. Methanol (MeOH) was used at UV-spectroscopy grade. Cyclohexane (Cy, Merck), chloroform, tetrahydrofuran (Centralchem, SR) and acetonitrile (Ac, Merck) were used at spectroscopy grade. Aldrich supplied 2,4-dinitrotoluene and 1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine (both 99% purity) were used as received.

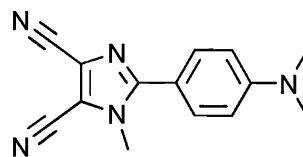
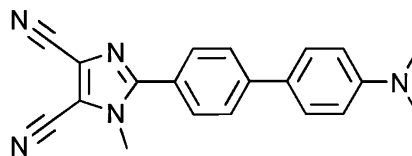
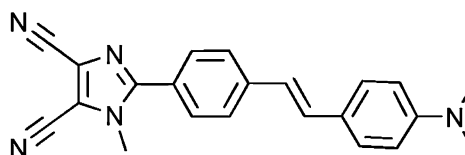
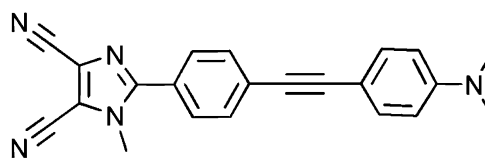
Polymer films doped with fluorophores (B1P, B2B, B3S and B4A) at a concentration of 0.002 mol kg⁻¹ were prepared by casting from solution. Films of polystyrene (PS) (Chemische Werke Huels, F.R.G.), and poly(methyl methacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting 1 ml of chloroform solution of polymer (5 g/100 ml) containing the desired amount of probe on a glass plate (28×35 mm). The solvent was slowly evaporated. Films of poly(vinylchloride) (PVC) (Neralit, Spolana Neratovice s.e., CR) were prepared in a similar way by casting from tetrahydrofuran solution. UV-VIS absorption spectra were taken on an UV 1650PC spectrometer (Shimadzu, Japan). Emission spectra were recorded on a RF-5301PC spectrofluorophotometer (Shimadzu, Japan). The fluorescence of the solutions was measured in 1×1 cm cuvette in the right-angle arrangement. The quantum yields were determined relative to anthracene in cyclohexane, chloroform or methanol. The fluorescence of the polymer films was taken in a front face

arrangement on the solid sample holder. The relative quantum yield of doped polymer films was determined with anthracene as the standard in the respective medium, using the quantum yields of anthracene in cyclohexane 0.25 [18]. The quantum yields of anthracene fluorescence in different media, which were determined by the comparison of the fluorescence of anthracene in cyclohexane and in various media, were found to be 0.20 in methanol and acetonitrile, and 0.11 in chloroform. In polymer matrices, the quantum yields were assumed to be 0.20 in PMMA, 0.16 in PS and 0.10 in PVC. The quantum yields in the solutions and films were corrected to different absorptions at the excitation wavelength [19]. The fluorescence spectra were taken using excitation into the maximum of the longest wavelength absorption band.

The fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, F.R.G.), which operates as a stroboscope. The excitation source was a nitrogen laser emitting at 337 nm and the emission was selected by a cut-off filter. The output signal of the boxcar integrator was digitized and transferred to the PC using a home-made program. The fluorescence decay curves were evaluated by a simple phase plane method [20] using J. Snyder's program based on Ref. [21]. The standard deviation $G^{1/2} = \left(\frac{\sum (I_{\text{exp}} - I_{\text{calc}})^2}{n} \right)^{1/2}$, where I_{exp} and I_{calc} are the intensity of the experimental and calculated emissions, respectively, was used to judge whether the decay was mono-exponential. The decay curve was assumed to be mono-exponential when $G^{1/2}$ was less than 5%. Alternatively, the fitting of fluorescence decay curves for a bi-exponential decay model was performed using the adapted FluoFit MatLab package [22].

Results and Discussion

The absorption spectra of the studied fluorophores in chloroform feature broad bands. The typical absorption spectra for B1P in various solvents are shown in Fig. 1. The absorption spectra for the other derivatives under study, B2B, B3S and B4A, exhibit similar features but are bathochromically shifted (see Supplement Figs. 1S, 2S and 3S). The relevant spectral data of the longest-wavelength absorption are summarized in Tables 1, 2, 3 and 4, and they lie between 300 and 400 nm. The longest-wavelength absorption bands were intense for all studied compounds in all solvents and polymer matrices (Tables 1, 2, 3 and 4). The studied compounds exhibited low solubility in cyclohexane, and therefore the decadic molar extinction coefficient was not determined in this solvent

Scheme 1 Chemical structures and names of investigated chromophores**B1P**2-(4-(*N,N*-dimethylaminophenyl)-1-methylimidazole-4,5-dicarbonitrile**B2P**2-(4'-(*N,N*-dimethylaminobiphenyl-4-yl)-1-methylimidazole-4,5-dicarbonitrile**B3S***(E)*-2-(4-(4-(*N,N*-dimethylaminostyryl)phenyl)-1-methylimidazole-4,5-dicarbonitrile**B4A**2-(4-(4-(*N,N*-dimethylaminophenylethynyl)phenyl)-1-methylimidazole-4,5-dicarbonitrile

(Tables 1, 2, 3 and 4). As a main spectral feature, a bathochromic shift was observed as a result of the elongation of the π -conjugated path separating the donor and the acceptor moieties. The expansion of the main B1P structure by one 1,4-phenylene, which is biphenyl linker in B2B, led to a redshift of about 10 to 25 nm, depending on the solvent used. The most redshifted longest-wavelength maxima (λ_{\max} of 376–397 nm) was observed for the more planar B3S in which the 4-(*N,N*-dimethylaminophenyl) moiety was separated by an additional styryl π -linker. On the other hand, the more electronegative π -linker in B4A

featuring a triple rather than a double bond caused a rather hypsochromic shift (λ_{\max} of 356–375 nm) compared to B3S [15, 22]. The introduction of an ethynylene bridge between the donor and acceptor in fluorophores is discussed also elsewhere [23, 24]. Application of different spacers leads to the modification of the extent of conjugation between donor and acceptor what allows tuning its ICT properties in final application. However, the largest shift of λ_{\max} for B3S was observed in chlorinated media (chloroform-383 nm and PVC matrix-397 nm) (Table 3). The longest-wavelength maxima of the simplest derivative B1P

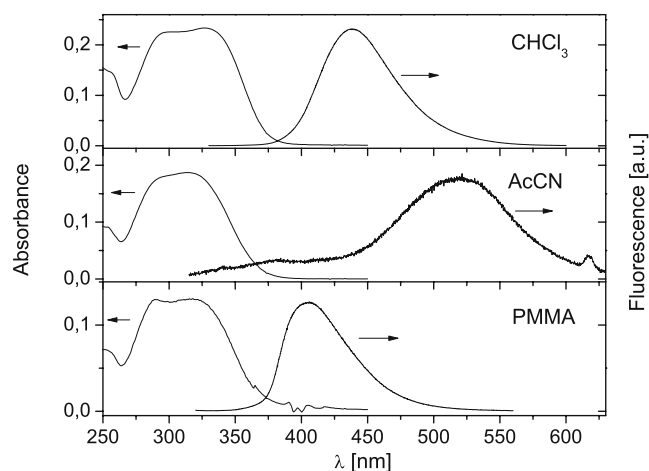


Fig. 1 Absorption and fluorescence spectra of B1P in chloroform (CHCl_3) and acetonitrile (Ac) at $10^{-5} \text{ mol L}^{-1}$ and PMMA at $0.002 \text{ mol kg}^{-1}$

was hypsochromically shifted in PVC compared to other media (λ_{max} of 326 nm in chloroform vs. 309 nm in PVC, Table 1).

The solutions of all compounds in chloroform exhibited intense fluorescence as broad band within the range of 437 to 500 nm (Fig. 1). The relevant data concerning fluorescence are given in Tables 1, 2, 3 and 4. Similar to absorption, the most redshifted fluorescence up to 500 nm was observed for B3S featuring an addition styryl π -linker. This derivative yielded less intense fluorescence in solutions, the lowest fluorescence quantum yield with anthracene as the standard ($\Phi = 0.16$) and the shortest lifetime of 0.7 ns (Table 3). The Stokes shifts in chloroform were rather large within the range of 6,000 to 8,000 cm^{-1} for all studied fluorophores.

B2B, B3S and B4A showed intense fluorescence with more than one maximum (vibrational structure) in non-polar cyclohexane (Tables 1, 2, 3 and 4). The intense fluorescence in cyclohexane was observed for fluorophores B1P, B2B and B4A, reaching $\Phi = 1$ for B2B. In cyclohexane, B3S showed fluorescence with maxima at 437 and 464 nm, low $\Phi = 0.17$ and the lowest Stokes shift of 3,000 to 6,000 cm^{-1} .

In both aprotic (acetonitrile) and protic (hydrogen-bonding methanol) polar solvents, the fluorescence was strongly quenched (Tables 1, 2, 3 and 4). The quantum yields varied within the range of 0.02 to 0.002. The remaining weak emission is redshifted up to 530 nm compared to non-polar cyclohexane and chloroform, exhibiting some shoulders within the range of 360 to 430 nm. However, in some cases, the observed weak fluorescence exhibited a maximum at a shorter wavelength below 500 nm (B1P in methanol, see Table 1). This phenomenon might indicate that the weak emission is due to some background fluorescence of the system fluorophore—solvent when fluorescence of the original fluorophore is completely quenched. The quantum yields under these conditions are loaded with considerable error ($\pm 100\%$). Because the signal intensity was rather low for our set-up, we were not able to measure the lifetimes of these fluorophores in polar solvents. The observed Stokes shifts in polar protic and aprotic solvents are spread over a wide range as a consequence of the observed shoulder. These data must be taken with some caution. Although the quantum yields of these fluorophores in polar solvents were not reliable due to low intensity, they indicate that the fluorescence of these fluorophores is more efficiently quenched by methanol than by acetonitrile. The extent of

Table 1 Spectral properties of fluorophore B1P in various media

| Medium | λ_A^a nm | $\log \epsilon^b$ $\text{L mol}^{-1} \text{ cm}^{-1}$ | λ_F^c nm | $\Delta\nu^d$ cm^{-1} | Φ^e | τ^f ns |
|--------------|---------------------|--|---------------------|-----------------------------------|----------|----------------|
| Cyclohexane | 323 | | 375 | 4,293 | 0.85 | 1.3 |
| Chloroform | 326 | 4.368 | 437 | 7,792 | 0.73 | 3.5 |
| Acetonitrile | 313 | 4.727 | 386s, 519 | 6,042 | 0.02 | |
| Methanol | 309 | 4.228 | 364s, 427 | 4,890 | 0.003 | |
| PS | 327 | 4.144 | 393 | 5,136 | 0.37 | 0.8 |
| PMMA | 318 | 4.116 | 406 | 6,816 | 0.21 | 1.6 |
| PVC | 309 | 4.293 | 425 | 8,833 | 0.16 | 1.7 |

^a Maxima of the longest-wavelength absorption

^b Molar decadic extinction coefficient

^c Fluorescent maxima, s—means shoulder

^d Stokes shift

^e Quantum yield of fluorescence using anthracene as standard

^f Lifetime of fluorescence

Table 2 Spectral properties of fluorophore B2B in various media

| Medium | λ_A^a nm | $\log \epsilon^b$ L mol ⁻¹ cm ⁻¹ | λ_F^c nm | ν^d cm ⁻¹ | Φ^e | τ^f ns |
|--------------|---------------------|---|---------------------|-----------------------------|----------|----------------|
| Cyclohexane | 333 | | 398,417 | 4,904 | 0.98 | 1.0 |
| Chloroform | 348 | 4.495 | 464 | 7,184 | 0.73 | 2.0 |
| Acetonitrile | 336 | 4.531 | 393s, 439 | 4,317 | 0.013 | |
| Methanol | 336 | 4.364 | 392s, 440 | 4,252 | 0.011 | |
| PS | 353 | 4.345 | 432 | 5,080 | 1.00 | 1.1 |
| PMMA | 344 | 4.149 | 434 | 6,028 | 0.27 | 1.3 |
| PVC | 357 | 4.508 | 452 | 5,887 | 0.64 | 1.6 |

^a Maxima of the longest-wavelength absorption

^b Molar decadic extinction coefficient

^c Fluorescent maxima, s—means shoulder

^d Stokes shift

^e Quantum yield of fluorescence using anthracene as standard

^f Lifetime of fluorescence

quenching expressed as the ratio of the quantum yields of fluorescence in chloroform to those in methanol or acetonitrile, was within the range of 37 to 293 for B1P/Ac and B4A/MeOH, respectively.

The fluorescence of fluorophores is rather intense in commonly used polymer matrices, being the most intense in PS. In this medium, the fluorescence quantum yields approached to 1 for B2B and B4A (Tables 2 and 4). The fluorescence of these fluorophores is less intense in PMMA, except for B3S. Because PMMA is widely used as a support matrix with generally weak interactions with the embedded fluorophores, the source of the weaker fluorescence in PMMA is not obvious. The longest-wavelength absorption and fluorescence maxima lie between two extremes of non-polar cyclohexane and polar

methanol. Whereas the spectral data of the fluorophores in PS approaches those in cyclohexane, the observed spectral data in PVC resemble those in chloroform. The lifetimes of the fluorophores in the polymer matrices are in the same range as those in the cyclohexane and chloroform. The lifetimes are slightly shorter in the PS matrix than in other matrices. Clearly, the derivatives under study yield intense fluorescence even in chlorinated media.

The derivative B3S featuring a styryl π -linker yielded fluorescence comparable to or weaker than anthracene in non-polar cyclohexane and chloroform. Its emission is negligible in polar solvents. This derivative yielded more intense fluorescence in polymer matrices than in solvents with low viscosity, and a fluorescence enhancement of about 4–5 was observed. These results indicate that the

Table 3 Spectral properties of fluorophore B3S in various media

| Medium | λ_A^a nm | $\log \epsilon^b$ L mol ⁻¹ cm ⁻¹ | λ_F^c nm | ν^d cm ⁻¹ | Φ^e | τ^f ns |
|--------------|---------------------|---|---------------------|-----------------------------|----------|----------------|
| Cyclohexane | 376 | | 437,464 | 3,712 | 0.17 | 0.7 |
| Chloroform | 383 | 4.271 | 500 | 6,110 | 0.16 | 0.7 |
| Acetonitrile | 380 | 4.696 | 428s, 530 | 2,951 | 0.002 | |
| Methanol | 378 | 4.642 | 514 | 6,999 | 0.002 | |
| PS | 390 | 4.289 | 476 | 4,633 | 0.52 | 0.9 |
| PMMA | 384 | 4.385 | 484 | 5,381 | 0.73 | 1.3 |
| PVC | 397 | 4.504 | 500 | 5,189 | 0.55 | 1.5 |

^a Maxima of the longest-wavelength absorption

^b Molar decadic extinction coefficient

^c Fluorescent maxima, s—means shoulder

^d Stokes shift

^e Quantum yield of fluorescence using anthracene as standard

^f Lifetime of fluorescence

Table 4 Spectral properties of fluorophore B4A in various media

| Medium | λ_A^a nm | $\log \epsilon^b$ $L \text{ mol}^{-1} \text{ cm}^{-1}$ | λ_F^c nm | ν^d cm^{-1} | Φ^e | τ^f ns |
|--------------|---------------------|---|---------------------|-----------------------------|----------|----------------|
| Cyclohexane | 372 | | 406,429 | 2,251 | 0.84 | 1.2 |
| Chloroform | 369 | 4.549 | 479 | 6,223 | 0.88 | 1.7 |
| Acetonitrile | 357 | 4.609 | 514 | 8,556 | 0.005 | |
| Methanol | 356 | 4.520 | 489 | 7,640 | 0.003 | |
| PS | 371 | 4.313 | 445 | 4,482 | 1.00 | 1.0 |
| PMMA | 365 | 4.356 | 450 | 5,175 | 0.42 | 1.3 |
| PVC | 375 | 4.607 | 466 | 5,207 | 0.83 | 1.5 |

^a Maxima of the longest-wavelength absorption

^b Molar decadic extinction coefficient

^c Fluorescent maxima, s—means shoulder

^d Stokes shift

^e Quantum yield of fluorescence using anthracene as standard

^f Lifetime of fluorescence

radiationless process is connected with rotation around the excited double bond in the excited singlet state. This rotation is partially or fully hindered in the polymer matrix. Therefore, B3S may serve as an indicator of microviscosity.

The lifetime of fluorophores under study of the emissive state lies in the range of 0.7–3.5 ns, typical for push-pull systems. This range is rather narrow and does not allow reasonable conclusions.

The strong solvent effects of polar solvents might be related to the non-emissive excited state featuring strong ICT from the electron-donating 4-(*N,N*-dimethylamino)phenyl- to the electron-accepting imidazole-4,5-dicarbonitrile unit. This transition state should be stabilized by polar aprotic solvents and stabilized even more efficiently by protic solvents, which should promote radiationless decay [25].

To gain increased insight into these radiationless processes, quenching with a known singlet state quencher such as the N-oxyl radical (1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine, TEMPOL) was compared to the quenching observed by the addition of polar solvents to the chloroform solution of the studied fluorophores. The fluorescence quench after the addition of TEMPOL in chloroform obeyed the Stern-Volmer relationship within a concentration range of 0.001 to 0.012 mol L⁻¹:

$$\Phi_0/\Phi = 1 + K_{SV}[Q] = 1 + k_q\tau[Q],$$

where the ratio Φ_0/Φ is the extent of quenching; K_{SV} is the Stern-Volmer constant, which is product of the bimolecular quenching rate constant and the lifetime $k_q * \tau$, and $[Q]$ is the quencher concentration.

For quenches B1P and B2B and TEMPOL as quenchers, an excellent linear behavior is observed (Fig 2). For B3S and B4A, which contain as linker double or triple bond, the

Stern-Volmer plot is less steep and the beginning the data are scattered. The relevant data are summarized in Table 5. The calculated bimolecular quenching rate constants are in the range typical for the diffusion-controlled bimolecular rate constant. These data show that the excited states of all fluorophores are effectively quenched, and the radiationless process is assumed to be promoted by the paramagnetic N-oxyl center.

Another type of quencher, 2,4-dinitrotoluene, which quenches via electron transfer, was also tested. This quencher strongly absorbs in the same region as the investigated fluorophores and, therefore, the separation of the screening and quenching effect was possible for B3S only (Supplement Fig. 4S). The value of $K_{SV} = 40.5 \text{ L mol}^{-1}$ is higher than those for TEMPOL, but it is loaded

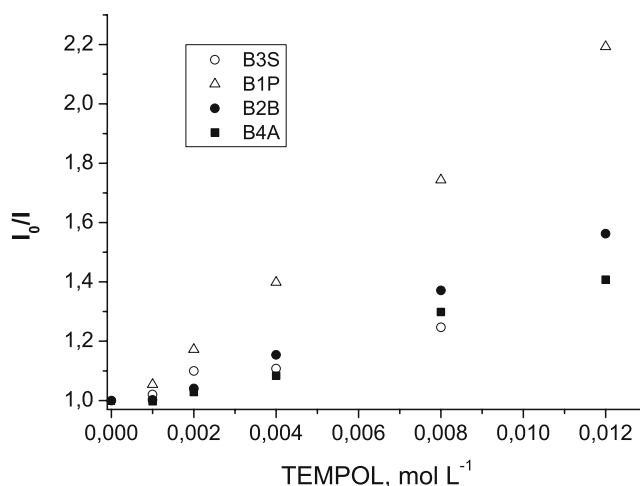


Fig. 2 Stern-Volmer plot of fluorescence quenching by TEMPOL in chloroform solution

Table 5 Quenching of fluorescence of fluorophores in chloroform by TEMPOL

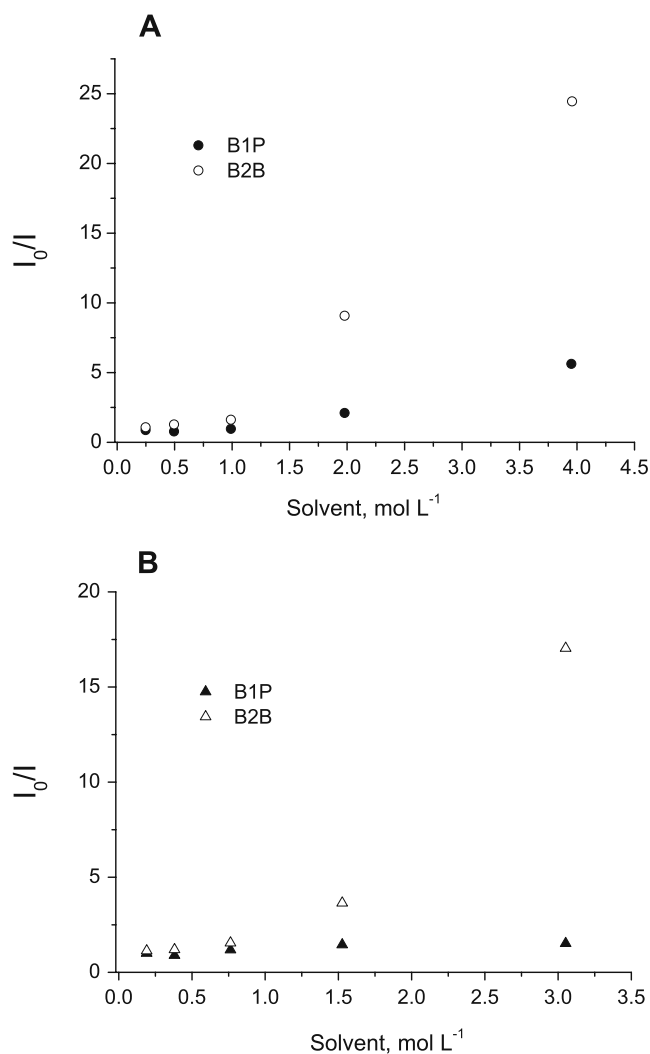
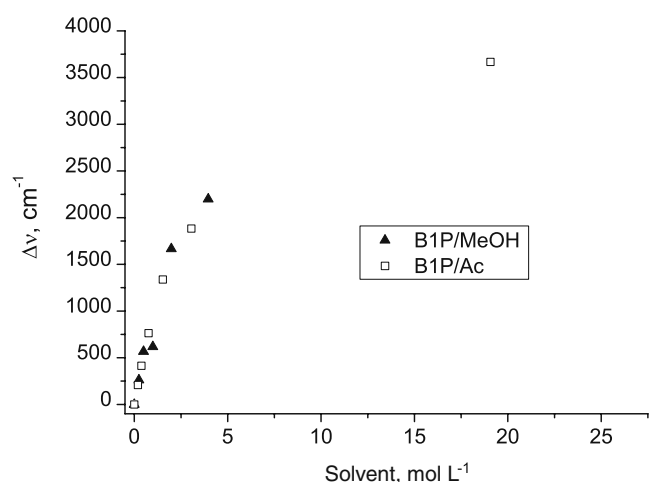
| Sample ^a | K_{SV}^b L mol ⁻¹ | A^c | r^d | τ^e ns | $k_q 10^{10f}$ L mol ⁻¹ s ⁻¹ |
|---------------------|-----------------------------------|-------|--------|----------------|---|
| B1P | 99.8 | 0.98 | 0.9986 | 3.5 | 2.85 |
| B2B | 49.6 | 0.97 | 0.9960 | 2.0 | 2.48 |
| B3S | 22.0 | 1.02 | 0.9477 | 0.7 | 3.14 |
| B4A | 32.6 | 0.90 | 0.9286 | 1.7 | 1.92 |

^a See Scheme 1 for the sample structures^b Stern-Volmer constant^c Abscissa on the y-axes^d Correlation coefficient^e Lifetime^f Diffusion controlled bimolecular quenching rate constant calculated as K_{SV}/τ

with a larger error. However, this value indicates that electron transfer can also be considered as a quenching mechanism.

Recently the mechanism of quenching by polar protic solvents like alcohols was analyzed in more detail [25]. The studied fluorophores can be divided into three groups. The first class of compounds, comprising substituted anthraquinones, underwent a drastic fluorescence quench following the Stern-Volmer plot. The second class of compounds, represented by substituted phthalimides, shows a substantial redshift without measurable quenching. The third class of compounds, represented by substituted coumarins, was not affected by polar ethanol at all. The fluorescence quench of our fluorophores by polar aprotic and protic solvents did not follow the Stern-Volmer relationship, as observed for the first class of compounds [25]. At polar solvent concentrations of 0.246 mol L⁻¹ (compared to the concentration of 0.001 mol L⁻¹ for quenching with TEMPOL), no distinct quenching was observed. However, the addition of larger amounts of polar solvent resulted in efficient fluorescence quenching. A typical course of the quenching caused by acetonitrile and methanol is given in Fig. 3a and b for B1P and B2B. This dependence is clearly not linear, being rather exponential instead. The extent of quenching is larger for methanol than for acetonitrile. The reason for this difference might be due to the ability to form hydrogen bonding of methanol, which can increase methanol concentration around excited fluorophore (which is in fact dipole) and consequently leads to the efficient quenching. The same dependence of the extent of quenching on polar solvent addition was observed for B3S and B4A as well. (Supplement Fig. 5S)

On the other hand, the addition of the same amount of polar solvent as used in the quenching experiments shifts the fluorescence maxima bathochromically. Surprisingly,

**Fig. 3** Effects of addition of methanol (MeOH) (a) and acetonitrile (Ac) (b) on the fluorescence of B1P and B2B in chloroform**Fig. 4** Fluorescence maxima shift for B1P in chloroform upon addition of methanol (MeOH) and acetonitril (Ac)

the same amount of polar solvent, which does not dramatically affect the fluorescence intensity, quite distinctly redshifts the fluorescence maxima. A plot of the redshift of the fluorescence maxima with addition of polar solvent, expressed as $\Delta\nu$ in cm^{-1} , on the concentration of polar solvent is given on Fig. 4 for B1P. This dependence has a different shape than that observed for the fluorescence quenching in the same concentration range (Fig. 3). The polar solvents affect the fluorescence spectra of the studied push-pull systems considerably. The same dependence of fluorescence redshift on the addition of polar solvent was also observed for B2P, B3S and B4A (Supplement Figs. 6S, 7S and 8S). These spectral data strongly indicate that the fluorescence spectra of push-pull systems are sensitive to the environment polarity, but not in linear manner. These data indicate that a higher concentration of polar solvents is needed to start radiationless process quenching, while a strong redshift is observed at lower polar solvent concentration.

As was indicated in some cases, the shift of the fluorescence maximum of the fluorophores under study is lower than those expected by extrapolation of $\Delta\nu$ on polar solvent addition. Compare the fluorescence maximum of B1P in acetonitrile (519 nm) and in methanol (427 nm) in Table 1. The red shift of $\Delta\nu$, $3,616 \text{ cm}^{-1}$, for B1P suits the dependence (Fig. 4), but the maximum fluorescence for methanol, 427 nm, lies under that of chloroform, 437 nm, and therefore does not mimic the dependence. The emission in this case is due to another system component. Methanol seems to be a more efficient quencher than acetonitrile. The discrepancy of the fluorescence maximum in methanol being at a lower wavelength than in chloroform, rather than at higher wavelength as expected from the dependence of $\Delta\nu$ on concentration, is more frequent for methanol than for acetonitrile. For B2P both, maxima in acetonitrile (439 nm) and methanol (440 nm) lie under those in chloroform (464 nm) (Table 2). For B3S, both fluorescence maxima (530 nm in acetonitrile, 514 nm in methanol) are above that in chloroform (500 nm) (see Table 3). For B4A, the maxima in acetonitrile (514 nm) and in methanol (489 nm) are above that in chloroform (479 nm) (Table 4).

Conclusions

New fluorophores based on imidazole-4,5-dicarbonitrile studied here showed interesting spectral properties that depended mainly on the type and length of the π -conjugated path separating the donor and acceptor moieties. Whereas the absorption spectra were moderately affected by the medium polarity, the fluorescence properties depended strongly on the solvent polarity. Dicarbonitrile-imidazole-based push-pull fluorophores as acceptor with dimethylaminophenyl donor yielded strong fluorescence in

non-polar and chlorinated solvents. Polar protic and aprotic solvents quenched the fluorescence (up to 290 times). Fluorophores embedded in polymer matrices exhibited weaker or comparable fluorescent behavior to non-polar solvents such as cyclohexane or chloroform.

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