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Photochemical, photophysical and electrochemical properties of six dansyl-based dyads†

Paola Ceroni,[a] Isaia Laghi,[a] Mauro Maestri,*[a] Vincenzo Balzani,[a] Sven Gestermann,[b] Marius Gorka[b] and Fritz Vögtle*[b]

[a] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2 I-40126, Bologna, Italy*
[b] *Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk Strasse 1, D-53121 Bonn, Germany*

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We have prepared six dyads containing a fluorescent propyldansylamide (PD) unit covalently linked to nitrobenzene (NB), naphthalene (NA), *trans*- and *cis*-azobenzene (*t*AZ and *c*AZ), 2,2′-bipyridine (BPY), and $[Ru(bpy)_3]^{2+}$ (RU) moieties. The photochemical, photophysical, and electrochemical properties of the dyads have been investigated in acetonitrile solution. In the PD-NB dyad, the fluorescence of the PD unit is quenched by electron transfer to the NB unit at 298 K, but it is not quenched in a rigid matrix at 77 K. In the PD-NA dyad, the fluorescence of the naphthalene unit is completely quenched by competing energy (80% efficiency) and electron transfer processes. In the case of PD-*t*AZ, the dansyl fluorescence is quenched without sensitization of the *trans* → *cis* photoisomerization reaction of the *t*AZ moiety, whereas in the PD-*c*AZ dyad the dansyl fluorescence quenching is accompanied by the sensitisation of the *cis* → *trans* photoisomerization of the *c*AZ moiety. In the PD-BPY dyad the fluorescence of the dansyl moiety is sensitized by the BPY unit; upon protonation or Zn^{2+} complexation of the BPY unit, however, the dansyl fluorescence is quenched by electron transfer. In the PD-RU dyad, the fluorescence of the dansyl unit is quenched by competing energy (25% efficiency) and electron transfer processes, whereas the emission of the RU moiety is unaffected.

Great interest is currently devoted to the study of the photochemical,[1] photophysical,[1,2] and electrochemical[3] properties of supramolecular systems for fundamental reasons as well as for the design of molecular-level devices[4] and machines.[5] The 5-dimethylamino-1-naphthalenesulfonamido chromophoric group (usually called dansyl) shows intense absorption bands in the near UV and a strong fluorescence in the visible region and it is extensively used for sensing or labelling purposes in supramolecular systems.[6] More recently, dansyl groups have also been appended at the periphery of poly(propylene amine) dendrimers capable of hosting metal ions and dyes in their interior.[7]

In order to better elucidate the excited state behavior of the dansyl chromophoric group, we have synthesized six novel dyads (Scheme 1) made of a propyldansylamide (PD) unit covalently linked to nitrobenzene (NB), naphthalene (NA), *trans*- and *cis*-azobenzene (*t*AZ and *c*AZ), 2,2′-bipyridine (BPY), and $[Ru(bpy)_3]^{2+}$ (RU) moieties and we have examined their photochemical, photophysical and electrochemical properties. Because of the great diversity of the units linked to the common dansyl chromophoric group, a variety of photophysical processes have been observed, such as sensitization of the dansyl fluorescence, quenching of the dansyl fluorescence by electron or energy transfer, and sensitized emission and reaction of the other component of the dyad.

Experimental

Synthesis and characterization of the dyads

All synthetic experiments were routinely carried out under a dry argon atmosphere. 2-Bromomethylnaphthalene, dansyl chloride, propylamine and *p*-toluidine were purchased from Aldrich, 4-nitrobenzyl bromide from Merck and *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II)dihydrate from Strem. 4-Bromomethylazobenzene and 5-bromomethyl-2,2′-bipyridine were prepared according to published procedures.[8,9]

NMR data were obtained on a Bruker AM 400 MHz (^1H NMR 400 MHz; ^{13}C NMR 100.6 MHz) spectrometer (as internal reference for ^1H and ^{13}C NMR spectra $CDCl_3$ signals were used and calculated for TMS). Mass spectroscopy was performed on MS-30 and MS-50 instruments (A.E.I., Manchester, UK) in EI mode and on a Concept 1H (KRATOS Analytical Ltd., Manchester, UK) in FAB mode.

5-Dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (PD). Propylamine (260 mg, 4.45 mmol) and 450 mg (4.45 mmol) of triethylamine were dissolved in 15 ml of dry dichloromethane under argon atmosphere. To the refluxing mixture a solution of 1.20 g (4.45 mmol) of dansyl chloride in 50 ml of dichloromethane was added dropwise. After stirring for 3 h under reflux the reaction mixture was stirred at 25 °C for 14 h. The solvent was removed *in vacuo* and the residue was collected in dichloromethane. After washing with water, aq. Na_2CO_3 and again with water three times the organic phase was dried with

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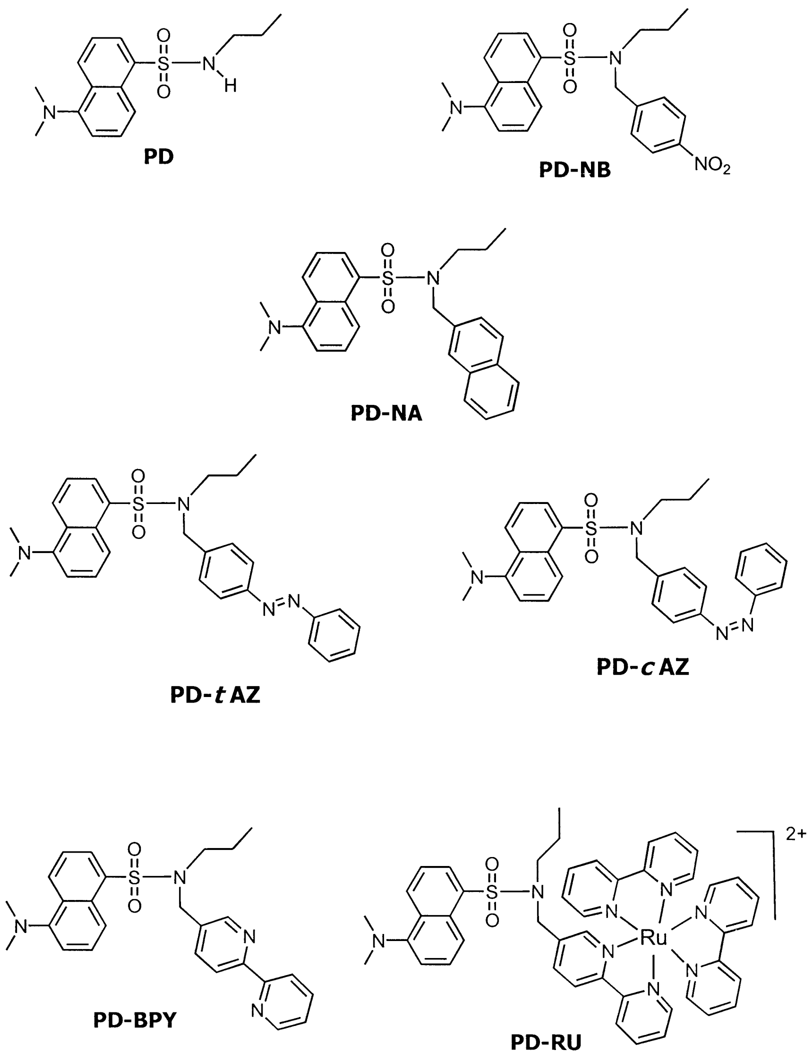
† Dedicated to Professor Alex von Zelewsky on the occasion of his 65th birthday.



Scheme 1 5-Dimethylaminonaphthalene-*N*-propyl-1-sulfonamide molecule (PD) and the investigated dyads.

Na_2SO_4. Further purification was achieved by column chromatography (SiO_2, 40–63 μm, dichloromethane) yielding 1.20 g (92%) of a bright yellow solid. M.p.: 95–96 °C. TLC (SiO_2): $R_f = 0.26$ (dichloromethane); ^{1}H-NMR: (400 MHz, C_6D_6, 25 °C) $\delta = 0.41$ [t, $^3J_{HH} = 7.38$ Hz, 3 H, $N(CH_2)_2CH_3$], 0.98 (sext, $^3J_{HH} = 7.28$ Hz, 2 H, $NCH_2CH_2CH_3$), 2.56 (q, $^3J_{HH} = 6.80$ Hz, 2 H, $NCH_2CH_2CH_3$), 4.69 (t, $^3J_{HH} = 6.15$ Hz, 1 H, SO_2NH), 6.84 (dd, $^3J_{HH} = 7.39$ Hz, $^4J_{HH} = 0.74$ Hz, 1 H, CH_{Dans}), 7.09 (dd, $^3J_{HH} = 7.39$ Hz, $^3J_{HH} = 8.62$ Hz, 1 H, CH_{Dans}), 7.42 (dd, $^3J_{HH} = 7.50$ Hz, $^3J_{HH} = 8.74$ Hz, 1 H, CH_{Dans}), 8.37 (dd, $^3J_{HH} = 7.38$ Hz, $^4J_{HH} = 1.23$ Hz, 1 H, CH_{Dans}), 8.42 (ddd, $^3J_{HH} = 8.62$ Hz, $^4J_{HH}$ and $^5J_{HH} = 0.99$ Hz, 1 H, CH_{Dans}), 8.76 (ddd, $^3J_{HH} = 8.62$ Hz, $^4J_{HH} = 0.74$ Hz, $^5J_{HH} = 0.99$ Hz, 1 H, CH_{Dans}); ^{13}C-NMR: (100.6 MHz, C_6D_6, 25 °C), $\delta = 11.1$ [$(CH_2)_2CH_3$], 23.2 ($CH_2CH_2CH_3$), 45.2 [$CH_2CH_2CH_3$ and $N(CH_3)_2$], 115.6, 120.2, 123.5 (CH_{Dans}), 127.7 (C_{Dans}), 128.6, 129.8, 130.2 (CH_{Dans}), 130.5, 136.5, 152.1 (C_{Dans}); EI-MS: *m*/*z* (%): calcd: for $C_{15}H_{20}N_2O_2S$ 292.1245; found: 292.1250 (31, M^+), 171.1 (100, $[Naph - NMe_2 + H]^+$), 154.1 (10), 128.0 (9).

4-Bromomethylazobenzene. A solution of 6.10 g (31.2 mmol) of 4-methylazobenzene, 5.60 g (31.2 mmol) of NBS and a few crystals of AIBN in CCl_4 was refluxed for 2 h and irradiated with a 300 W light source. The precipitated succinimide was filtered off and the filtrate was evaporated under reduced pressure. Recrystallization from toluene yielded 4.0 g (47%) of an orange solid. M.p.: 114 °C. ^{1}H-NMR: (250 MHz, $CHCl_3$, 25 °C) $\delta = 4.55$ (s, 2H, CH_2), 7.40–7.60 (m, 5H, ar. H), 7.85–7.98 (m, 4H, ar. H); ^{13}C-NMR: (62.9 MHz, $CHCl_3$, 25 °C) $\delta = 32.8$ (CH_2), 122.9 (CH, ar.), 123.2 (CH, ar.), 129.1 (CH, ar.), 129.9 (CH, ar.), 131.2 (CH, ar.), 140.5 (C_q, ar.), 152.3 (C_q, ar.), 152.5 (C_q, ar.); EI-MS: *m*/*z* (%): calcd for $C_{13}H_{11}N_2Br$ 274.01; found: 274 (M^+,10), 195 ($[M - Br]^+$, 13), 90 (Ph^+, 45).

***N*-(Azobenzene-4-ylmethyl)-5-dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (PD-*t*AZ).** 5-Dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (80 mg, 0.27 mmol) and 210 mg of potassium carbonate were dissolved in 10 ml of dry DMF. To this suspension a solution of 80 mg (0.29 mmol) of *trans*-azobenzene-4-methyl bromide in 10 ml of DMF was added dropwise. The mixture was stirred at 25 °C for 24 h under argon atmosphere. After filtering the undissolved K_2CO_3 the solvent was removed *in vacuo* and the residue was collected in dichloromethane. After washing with water, aq. Na_2CO_3 and again with water the organic phase was dried with Na_2SO_4. Further purification was achieved by column chromatography (SiO_2, 63–100 μm, chloroform–ethyl acetate 60 : 1), yielding 125 mg (94%) of an intense orange solid. TLC (SiO_2): $R_f = 0.22$ (chloroform–ethyl acetate 80 : 1); ^{1}H-NMR: (400 MHz, $CDCl_3$, 25 °C), $\delta = 0.66$ (t, $^3J_{HH} = 7.4$ Hz, 3 H, CH_3), 1.42 (sext, $^3J_{HH} = 7.5$ Hz, 2 H, $CH_2CH_2CH_3$), 2.86 [s, 6 H, $N(CH_3)_2$], 3.23 (t, $^3J_{HH} = 7.8$ Hz, 2 H, $CH_2CH_2CH_3$), 4.54 (s, 2 H, NCH_2Ar), 7.18 (d, $^3J_{HH} = 7.1$ Hz, 1 H, CH_{Dans}) 7.31 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CH_{ar}), 7.44–7.51 (m, 4 H, 1 CH_{Dans}, 3

CH$_{ar}$) 7.57 (dd, $^3J_{HH} = 8.6$ Hz and $^3J_{HH} = 7.6$ Hz, 1 H, CH$_{Dans}$), 7.78 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CH$_{ar}$), 7.89 (dd, $^3J_{HH} = 8.2$ Hz and $^4J_{HH} = 1.4$ Hz, 2 H, CH$_{ar}$), 8.26 (dd, $^3J_{HH} = 7.3$ Hz and $^4J_{HH} = 1.1$ Hz, 1 H, CH$_{Dans}$), 8.38 (d, $^3J_{HH} = 8.9$ Hz, 1 H, CH$_{Dans}$), 8.53 (d, $^3J_{HH} = 8.4$ Hz, 1 H, CH$_{Dans}$); ^{13}C-NMR: (100.6 MHz, CDCl$_3$, 25 °C) $\delta = 10.9$, 20.8, 45.3 [N(CH$_3$)$_2$], 48.6 (SO$_2$NCH$_2$Ar), 50.3 (SO$_2$NCH$_2$-Ar), 115.0, 119.3, 122.7, 122.8, 123.0, 128.0, 128.8, 128.9, 129.7, 129.8, 129.9, 130.3, 130.9, 134.9, 139.3, 151.6, 151.8, 152.4 (C$_{ar}$); EI-MS: m/z (%): calcd for $C_{28}H_{30}N_4O_2S$ 486.63; found: 486.2 (85, M$^+$), 171.0 (100, [C$_{10}$H$_6$N(CH$_3$)$_2$ + H]$^+$).

***N*-(2-Naphthalenemethyl)-5-dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (PD-NA).** 5-Dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (102 mg, 0.35 mmol) and 210 mg of potassium carbonate were dissolved in 10 ml of dry DMF. To this suspension a solution of 77 mg (0.35 mmol) of 2-bromomethylnaphthalene in 20 ml of DMF was added dropwise. The mixture was stirred at 25 °C for 1 day under argon atmosphere. After filtering the undissolved K$_2$CO$_3$ the solvent was removed *in vacuo* and the residue was collected in dichloromethane. After washing with water, aq. Na$_2$CO$_3$ and again with water the organic phase was dried with Na$_2$SO$_4$. Further purification was achieved by column chromatography (SiO$_2$, 40–60 µm, dichloromethane) yielding 130.1 mg (86%) of a bright yellow solid. M.p.: 91–92 °C. TLC (SiO$_2$): $R_f = 0.38$ (dichloromethane); ^{1}H-NMR: (400 MHz, CDCl$_3$, 25 °C), $\delta = 0.67$ (t, $^3J_{HH} = 7.38$ Hz, 3 H, CH$_3$), 1.44 (sext, $^3J_{HH} = 7.48$ Hz, 2 H, CH$_2$*CH*$_2$CH$_3$), 2.90 [s, 6 H, N(CH$_3$)$_2$], 3.23 (t, $^3J_{HH} = 7.63$ Hz, 2 H, *CH*$_2$CH$_2$CH$_3$), 4.63 (s, 2 H, NCH$_2$Naph), 7.23 and 7.25 (d, $^3J_{HH} = 8.86$ Hz and $^3J_{HH} = 7.63$ Hz, je 1 H, CH$_{Naph}$ and CH$_{Dans}$), 7.44 (dd, $^3J_{HH} = 6.15$ and 3.20 Hz, 2 H, CH$_{Naph}$), 7.51 (dd, $^3J_{HH} = 8.61$ Hz and $^3J_{HH} = 7.14$ Hz, 1 H, CH$_{Dans}$), 7.51 (s, 1 H, CH$_{Naph}$), 7.60 (pt, $^3J_{HH} = 8.24$ Hz, 1 H, CH$_{Dans}$), 7.63 (dd, $^3J_{HH} = 6.03$ Hz and $^4J_{HH} = 3.81$ Hz, 1 H, CH$_{Naph}$), 7.69 (d, $^3J_{HH} = 8.37$ Hz, 1 H, CH$_{Naph}$), 7.77 (dd, $^3J_{HH} = 5.78$ Hz and $^4J_{HH} = 3.57$ Hz, 1 H, CH$_{Naph}$), 8.29 (d, $^3J_{HH} = 8.37$ Hz, 1 H, CH$_{Dans}$), 8.43 (d, $^3J_{HH} = 8.61$ Hz, 1 H, CH$_{Dans}$), 8.56 (d, $^3J_{HH} = 8.37$ Hz, 1 H, CH$_{Dans}$); ^{13}C-NMR: (100.6 MHz, CDCl$_3$, 25 °C), $\delta = 11.1$, 20.9, 45.5 [N(CH$_3$)$_2$], 48.4, 50.7, 115.3, 119.9, 123.3, 126.0 (C$_{Naph}$), 126.1 (C$_{Naph}$), 126.2 (C$_{Naph}$), 127.2 (C$_{Naph}$), 127.6 (C$_{Naph}$), 127.7 (C$_{Naph}$), 128.1, 128.3 (C$_{Naph}$), 130.0, 130.1, 130.2, 130.3, 132.8 (C$_{Naph}$), 133.2 (C$_{Naph}$), 133.7 (C$_{Naph}$), 135.3, 151.7; EI-MS: m/z (%): calcd for $C_{26}H_{28}N_2O_2S$ 432.1871; found: 432.1873 (17, M$^+$), 198.1 (10), 171.1 (100, [C$_{10}$H$_6$N(CH$_3$)$_2$ + H]$^+$), 141.1 (28).

***N*-(4-Nitrobenzyl)-5-dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (PD-NB).** 5-Dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (100 mg, 0.34 mmol) and 210 mg of potassium carbonate were dissolved in 5 ml of dry DMF. To this suspension a solution of 81.3 mg (0.38 mmol) of 4-nitrobenzyl bromide in 30 ml of DMF was added dropwise. The mixture was stirred at 25 °C for 15 h under argon atmosphere. After filtering the undissolved K$_2$CO$_3$ the solvent was removed *in vacuo* and the residue was collected in dichloromethane. After washing with water, aq. Na$_2$CO$_3$ and again with water the organic phase was dried with Na$_2$SO$_4$. Further purification was achieved by column chromatography (SiO$_2$, 60–100 µm, dichloromethane) yielding 65.5 mg (45%) of a green-yellow solid. TLC (SiO$_2$): $R_f = 0.26$ (dichloromethane); ^{1}H-NMR: (400 MHz, CDCl$_3$, 25 °C), $\delta = 0.65$ (t, $^3J_{HH} = 7.4$ Hz, 3 H, CH$_3$), 1.36 (sext, $^3J_{HH} = 7.5$ Hz, 2 H, CH$_2$*CH*$_2$CH$_3$), 2.89 [s, 6 H, N(CH$_3$)$_2$], 3.19 (t, $^3J_{HH} = 7.8$ Hz, 2 H, *CH*$_2$CH$_2$CH$_3$), 4.56 (s, 2 H, N*CH*$_2$C$_6$H$_5$), 7.20 (d, $^3J_{HH} = 7.4$ Hz, 1 H, CH$_{Dans}$), 7.34 (d, $^3J_{HH} = 8.8$ Hz, 2 H, CH$_{ar}$), 7.50 (dd, $^3J_{HH} = 8.4$ Hz and $^3J_{HH} = 7.4$ Hz, 1 H, CH$_{Dans}$), 7.56 (dd, $^3J_{HH} = 8.6$ Hz and $^3J_{HH} = 7.6$ Hz, 1 H, CH$_{Dans}$), 8.05 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CH$_{ar}$), 8.22 (dd, $^3J_{HH} = 7.4$ Hz and $^4J_{HH} = 1.2$ Hz, 1 H, CH$_{Dans}$), 8.29 (d, $^3J_{HH} = 8.6$ Hz, 1 H, CH$_{Dans}$), 8.55 (d, $^3J_{HH} = 8.4$ Hz, 1 H, CH$_{Dans}$); ^{13}C-NMR: (100.6 MHz, CDCl$_3$, 5 °C), $\delta = 10.9$, 21.0, 45.3 [N(CH$_3$)$_2$], 49.2, 50.2, 115.6, 119.2, 123.1, 123.5 (2 CH$_{ar}$), 128.2, 128.6 (2 CH$_{ar}$), 129.8, 129.9, 130.0, 130.6, 134.6, 144.1 (C$_{ar}$), 147.2 (C$_{ar}$), 151.6; EI-MS: m/z (%): calcd for $C_{22}H_{26}N_3O_4S$ 427.1566, found: 427.1573 (14, M$^+$), 171.1 (100, [C$_{10}$H$_6$N(CH$_3$)$_2$ + H]$^+$).

***N*-(2,2′-Bipyridin-5-ylmethyl)-5-dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (PD-BPY).** 5-Dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (50 mg, 0.17 mmol) and 200 mg of potassium carbonate were dissolved in 10 ml of dry DMF. To this suspension a solution of 54 mg (0.22 mmol) of 5-bromomethyl-2,2-bipyridine in 40 ml of DMF was added dropwise. The mixture was stirred at 25 °C for 3 days under argon atmosphere. After filtering the undissolved K$_2$CO$_3$ the solvent was removed *in vacuo* and the residue was collected in dichloromethane. After washing with water, aq. Na$_2$CO$_3$ and again with water the organic phase was dried with Na$_2$SO$_4$. After removal of the solvent under reduced pressure the residue was chromatographed twice (SiO$_2$, 40–60 µm, dichloromethane–methanol 20 : 1 and SiO$_2$, 40–60 µm, petroleum ether (40–60)–methanol–triethylamine 15 : 1 : 1) to yield 50.5 mg (64%) of a bright yellow solid. TLC (SiO$_2$): $R_f = 0.20$ (dichloromethane–methanol 20 : 1); ^{1}H-NMR: (400 MHz, CDCl$_3$, 25 °C) $\delta = 0.67$ (t, $^3J_{HH} = 7.4$ Hz, 3 H, CH$_3$), 1.42 (sext, $^3J_{HH} = 7.6$ Hz, 2 H, CH$_2$*CH*$_2$CH$_3$), 2.86 [s, 6 H, N(CH$_3$)$_2$], 3.20 (t, $^3J_{HH} = 7.9$ Hz, 2 H, *CH*$_2$CH$_2$CH$_3$), 4.51 (s, 2 H, NCH$_2$Bpy), 7.18 (d, $^3J_{HH} = 7.4$ Hz, 1 H, CH$_{Dans}$), 7.28 (ddd, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 4.8$ Hz, $^4J_{HH} = 1.1$ Hz, 1 H, CH$_{Bpy}$), 7.50 (dd, $^3J_{HH} = 8.4$ Hz and $^3J_{HH} = 7.4$ Hz, 1 H, CH$_{Dans}$), 7.56 (dd, $^3J_{HH} = 8.5$ Hz and $^3J_{HH} = 7.5$ Hz, 1 H, CH$_{Dans}$), 7.58 (dd, $^3J_{HH} = 8.0$ Hz and $^4J_{HH} = 2.2$ Hz, 1 H, CH$_{Bpy}$), 7.78 (td, $^3J_{HH} = 7.7$ Hz and $^4J_{HH} = 1.8$ Hz, 1 H, CH$_{Bpy}$), 8.22 (d, $^3J_{HH} = 7.9$ Hz, 1 H, CH$_{Bpy}$), 8.24 (dd, $^3J_{HH} = 7.4$ Hz and $^4J_{HH} = 1.2$ Hz, 1 H, CH$_{Dans}$), 8.31 (m, 2 H, CH$_{Bpy}$ and CH$_{Dans}$), 8.43 (d, $^4J_{HH} = 1.7$ Hz, 1 H, CH$_{Bpy}$), 8.52 (d, $^3J_{HH} = 8.4$ Hz, 1 H, CH$_{Dans}$), 8.64 (dq, $^3J_{HH} = 4.8$ Hz and $^4J_{HH} = 0.8$ Hz, 1 H, CH$_{Bpy}$); ^{13}C-NMR: (100.6 MHz, CDCl$_3$, 25 °C), $\delta = 11.0$, 21.0, 45.3 [N(CH$_3$)$_2$], 48.0, 48.6, 115.2, 119.2, 120.8 (CH$_{Bpy}$), 121.0 (CH$_{Bpy}$), 123.1, 123.8 (CH$_{Bpy}$), 128.2, 129.9, 130.0, 130.1, 130.6, 131.9 (CH$_{Bpy}$), 134.7, 136.9 (CH$_{Bpy}$), 137.0 (CH$_{Bpy}$), 148.8 (CH$_{Bpy}$), 149. (C$_{Bpy}$), 151.8, 155.6 (C$_{Bpy}$), 155.7 (C$_{Bpy}$); EI-MS: m/z (%): calcd for $C_{26}H_{28}N_4O_2S$ 460.1933; found: 460.1932 (27, M$^+$), 445.2 (20, [M − CH$_3$]$^+$), 431.2 (30, [M − C$_2$H$_5$]$^+$), 267.1 (40), 226.1 (65, [M − C$_{12}$H$_{10}$NO$_2$S]$^+$), 169.1 (33), 101.1 (22), 86.1 (100), 50.1 (41).

[{*N*-(2,2′-Bipyridin-5-ylmethyl)-5-dimethylaminonaphthalene-*N*-propyl-1-sulfonamide}] bis(2,2′-bipyridine)]ruthenium(II) bis(hexafluorophosphate) (PD-RU). A suspension of 56 mg (0.12 mmol) of *N*-(2,2′-bipyridin-5-ylmethyl)-5-dimethylaminonaphthalene-*N*-propyl-1-sulfonamide and 60 mg of *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate in 5 ml of ethylene glycol and 1.5 ml of ethanol was heated under reflux twice for 2 min in a microwave oven at 600 W. The completion of complexation was controlled *via* TLC (acetonitrile–water–methanol–potassium nitrate 40 : 10 : 10 : 1). After cooling the now orange reaction mixture was treated with 20 ml of water and 2.0 g of ammonium hexafluorophosphate. The voluminous precipitate was filtered off and washed with water and diethyl ether to yield 91.7 g (87%) of an intense orange solid, melting at 183–185 °C with decomposition. TLC (SiO$_2$): $R_f =$ (acetonitrile–methanol–water–potassium nitrate 40 : 10 : 10 : 1); ^{1}H-NMR: (250 MHz, CD$_3$CN, 25 °C) $\delta = 0.42$ (t, $^3J_{HH} = 7.3$ Hz, 3 H, CH$_3$), 0.99 (psext, $^3J_{HH} = 7.4$ Hz, 2 H, CH$_2$*CH*$_2$CH$_3$), 2.85 [s, 6 H, N(CH$_3$)$_2$], 2.98 (t, $^3J_{HH} = 7.6$ Hz, 2

H, CH_2CH$_2$CH$_3$), 4.42 (q, $^2J_{HH} = 16.8$ Hz, 2 H, SO$_2$NCH$_2$-Bpy), 7.25 (d, $^3J_{HH} = 7.5$ Hz, 1 H, CH$_{Dans}$), 7.39 (t, $^3J_{HH} = 6.1$ Hz, 5 H, CH$_{Bpy}$), 7.52 (dd, $^3J_{HH} = 8.1$ Hz, 1 H, CH$_{Dans}$), 7.56 (pt, $^3J_{HH} = 8.3$ Hz, 1 H, CH$_{Dans}$), 7.73 (m, 5 H, CH$_{Bpy}$), 7.89 (d, $^4J_{HH} = 2.0$ Hz, 1 H, CH$_{Bpy}$), 7.92 (dd, $^3J_{HH} = 7.3$ Hz and $^4J_{HH} = 1.5$ Hz, 1 H, CH$_{Bpy}$), 8.01–8.13 (br m, 6 H, 5 CH$_{Bpy}$ and 1 CH$_{Dans}$), 8.37–8.52 (br m, 8 H, 6 CH$_{Bpy}$ and 2 CH$_{Dans}$); ^{13}C-NMR: (100.6 MHz, CD$_3$CN, 25 °C) $\delta = 11.2$, 22.6, 46.0, 49.6, 51.7, 116.8, 120.7, 124.8, 125.4, 125.5, 125.6, 128.6, 128.7, 128.8, 129.4, 129.8, 130.6, 130.8, 131.1, 135.9, 138.0, 138.9, 139.0, 139.1, 139.4, 152.2, 152.6, 152.8, 152.9, 57.1, 157.8, 158.0, 158.0, 158.1, 158.2; FAB-MS: *m*/*z* (%): 1019.3 (10, $[M - PF_6]^+$), 874.2 (10, $[M - 2PF_6]^+$).

Photochemical, photophysical and electrochemical experiments

The absorption spectra and photophysical properties (fluorescence spectra, quantum yields, and excited state lifetimes) have been studied in air-equilibrated CH$_2$Cl$_2$ or methylcyclohexane solutions at 298 K and in butyronitrile or methylcyclohexane at 77 K. Absorption spectra were recorded on a Perkin Elmer Lambda16 spectrophotometer. Luminescence spectra were obtained with a Perkin Elmer LS 50 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Luminescence lifetimes were measured by time-correlated single-photon counting equipment (Edinburgh instruments DS199, D$_2$ lamp). Luminescence quantum yields were measured with a Perkin Elmer LS 50 spectrofluorimeter, following the method described by Demas and Crosby[10a] using $[Ru(bpy)_3]^{2+}$ ($\Phi = 2.8 \times 10^{-2}$ in aerated water),[10b] quinine sulfate ($\Phi = 0.55$ in aerated water–1N H$_2$SO$_4$ solution)[10c] or naphthalene ($\Phi = 0.23$) in deaerated cyclohexane[10d] as standards. The estimated experimental error is 2 nm on the band maximum, 5% on the molar absorption coefficient, 10% on the fluorescence quantum yield, 5% on the fluorescence lifetime, and 15% on the photoisomerization quantum yield.

In continuous irradiation experiments, light excitation was performed by a medium pressure mercury lamp. Interference filters (Oriel) were used to select a narrow spectral range with $\lambda_{max} = 313$, 365 or 435 nm. The irradiated solution was contained in a 1 cm spectrophotometric cell. The intensity of the incident light (9.1×10^{-8} einstein min^{-1} at 313 nm, 1.3×10^{-7} einstein min^{-1} at 365 nm, and 2.4×10^{-6} einstein min^{-1} at 435 nm) was measured by a ferrioxalate actinometer.[11]

The concentration of the compounds examined in the photochemical and photophysical experiments was in the range 1–3 × 10^{-5} M.

^{1}H NMR spectroscopy experiments, related to the *cis*/*trans* isomerization of aza compounds, were performed on a Varian Gemini 300 spectrometer at 298 K in *ca.* 10^{-3} M CD$_3$CN solution by using TMS as a reference. Photostationary composition and conversion percentages were determined by integration of the signals in the ^{1}H NMR spectra recorded before and after the irradiation.

The electrochemical experiments were carried out in argon-purged DMF or MeCN (Romil Hi-Dry^{TM}) solutions at 298, 228 or 219 K (by employing a liquid N$_2$–EtOH low-temperature bath) with an EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.08 cm^2, Amel); its surface was routinely polished with a 0.05 μm alumina–water slurry on a felt surface, immediately before use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and a silver wire was employed as a quasi-reference electrode (AgQRE). The potentials reported are referred to SCE by measuring the AgQRE potential with respect to ferrocene. The concentration of the compounds examined was of the order of 5 × 10^{-4} M; 0.05 M tetraethylammonium hexafluorophosphate (TEAPF$_6$) and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) were added to MeCN and DMF solutions, respectively, as supporting electrolytes. Cyclic voltammograms were obtained with scan rates in the range 0.05–10 V s^{-1}. The number of electrons exchanged in each process was estimated by comparing the current intensity of the corresponding CV wave with that observed for the monoelectronic oxidation of ferrocene, after correction for differences in the diffusion coefficients.[12] The experimental error on the potential values was estimated to be ±10 mV. The CV simulations were carried out by the program Antigona developed by Dr Loic Möttier.[13] All the electron transfer processes were considered fast in the simulation and the chemical rate constants were chosen so as to obtain a visual best fit over a 100-fold variation of scan rate.

Results and discussion

Component units

The absorption and fluorescence spectra in acetonitrile solution at 298 K of the parent 5-dimethylaminonaphthalene-*N*-propyl-1-sulphonamide molecule (PD, Scheme 1), are shown in Fig. 1(a). The two relatively intense absorption bands in the near UV region are due to $\pi \rightarrow \pi^*$ ($\lambda_{max} = 250$ nm) and $n \rightarrow \pi^*$ ($\lambda_{max} = 340$ nm) transitions and the strong fluorescence band with $\lambda_{max} = 510$ nm ($\Phi = 0.30$, $\tau = 12$ ns; Table 1) originates from the singlet nπ^* excited state.[14] From the onset of the emission band in acetonitrile at room temperature, the E_{00} value of the fluorescent excited state is estimated to be 2.8 eV. The fluorescence band moves to higher energy [Fig. 1(a)] in a rigid matrix ($\lambda_{max} = 466$ nm in butyronitrile at 77 K) or on decreasing solvent polarity ($\lambda_{max} = 450$ nm in cyclohexane at 298 K). No phosphorescence is observed, even in a rigid matrix at 77 K. Upon acid titration of the amine group, the low energy nπ^* absorption and emission bands disappear with the

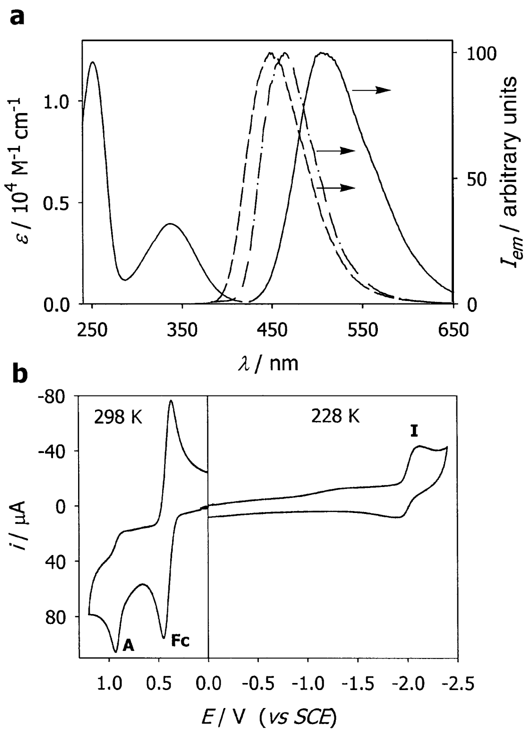


Fig. 1 (a) Full line: absorption and fluorescence spectra in acetonitrile solution at 298 K of 5-dimethylaminonaphthalene-*N*-propyl-1-sulfonamide (PD). The fluorescence spectra in butyronitrile at 77 K (dashed-dotted line) and in cyclohexane at 298 K (dashed line) are also shown. (b) Cyclic voltammogram of PD in acetonitrile–TEAPF$_6$ solution.

Table 1 Emission data of the dyads and some model compounds in air-equilibrated solutions ($\lambda_{ex} = 340$ nm, unless otherwise noted)

	298 K[a]			77 K[b]	
	λ_{max}/nm	ϕ_{em}	τ/ns	λ_{max}/nm	τ/ns
PD	510	0.30	12.0	466	15.8
PD-NB	520	$< 0.01^c$	12.0^c	466	12.8
PD-NA	525	0.28	12.4	464	15.3
PD-*t*AZ	520	$< 0.01^c$	12.3^c	—	—
PD-*c*AZ	520	$< 0.01^c$	12.3^c	—	—
PD-BPY	520	0.26	12.7	463	14.9
PD-RU	520	$< 0.01^c$	12.3^c		
	615	0.013^d	176	580	5700

[a] In acetonitrile solution. [b] In butyronitrile solution. [c] Residual emission, lilkely due to an impurity of free dansyl species. [d] $\lambda_{ex} = 450$ nm.

concomitant appearance of absorption and emission bands at 286 and 330 nm, respectively.[7a]

Fig. 1(b) shows the cyclic voltammogram obtained for PD in acetonitrile solution. Beside the peak of the internal ferrocene reference compound, one can observe an oxidation and a reduction process. Both processes are monoelectronic and electrochemically reversible, but chemically irreversible because of reactions involving the oxidized and reduced species. Reversibility increases with increasing scan rate and decreasing temperature. The reduction process becomes fully reversible at 228 K ($E_{1/2} = -2.02$ V, Table 2). In the case of the oxidation process, a simulation procedure[13] (according to an EC mechanism) yields $E_{1/2} = +0.9$ V and a value of about 10 s^{-1} for the rate constant of the reaction involving the oxidized species. The oxidation process involves the amine nitrogen, as shown by the fact that tertiary aliphatic amines are oxidized at similar potential values[15] and by the disappearance of the peak upon addition of acid. The reduction process should involve the naphthalenesulfonamido site of dansyl.

The photochemical, photophysical and electrochemical properties of the model compounds of the other components of the dyads will be illustrated when discussing the respective dyad. Most of the photophysical and electrochemical data of the examined compounds are gathered in Tables 1 and 2.

Energetics of the intercomponent processes

As we will see below, electronic interaction between the dansyl moiety and the other unit contained in the dyad leads to the occurrence of energy and/or electron transfer processes. The quenching of an excited state A* by energy transfer to a species B is thermodynamically allowed [$\Delta G < 0$, eqn. (1)] when the energy of the donor excited state is higher than that of the acceptor excited state (the excited state energy is usually expressed by the zero-zero spectroscopic energy, E_{00})[1a]:

$$\Delta G \sim -[E_{00}(\mathrm{A}^*) - E_{00}(\mathrm{B}^*)] \tag{1}$$

The free energy change for the quenching by electron transfer is given by[1a,16]:

$$\Delta G \sim F[E^\circ(\mathrm{A}^+/\mathrm{A}) - E^\circ(\mathrm{B}/\mathrm{B})] - E_{00}(\mathrm{A}^*) - w$$

$$\text{(oxidative quenching)} \tag{2}$$

$$\Delta G \sim F[-E^\circ(\mathrm{A}/\mathrm{A}^-) + E^\circ(\mathrm{B}^+/\mathrm{B})] - E_{00}(\mathrm{A}^*) - w$$

$$\text{(reductive quenching)} \tag{3}$$

where F is the Faraday constant, $E^\circ(\mathrm{A}^+/\mathrm{A})$, $E^\circ(\mathrm{A}/\mathrm{A}^-)$, $E^\circ(\mathrm{B}^+/\mathrm{B})$ and $E^\circ(\mathrm{B}/\mathrm{B}^-)$ are the standard potentials of the ground state couples, E_{00} is the zero-zero spectroscopic energy and w is the coulombic work term, which can be neglected in polar solvents.

Table 2 Electrochemical potentials (in V *vs.* SCE 298 K)[a]

	B	A	I	II	III
PD[b]		+ 0.90	− 2.02		
PD-NB[b]		$+ 0.92^c$	− 1.10		
		$+ 0.90^{c,d}$	$- 1.10^d$		
PD-NA[b]		$+ 0.90^b$			
PD-*t*AZ[b]		$+ 0.90^c$	− 1.36		
		$+ 0.92^{c,d}$	$- 1.30^d$		
PD-*c*AZ[b]		$+ 0.90^c$	− 1.35		
			$- 1.28^d$		
PD-BPY[e]			$- 2.0^c$		
		$+ 0.94^{c,f}$	$- 2.03^f$		
PD-RU	$+ 1.31^{b,c}$	$+ 0.95^{b,c}$	$- 1.30^e$	$- 1.49^{c,e}$	
			$- 1.37^{e,f}$	$- 1.52^{e,f}$	$- 1.76^{e,f}$

[a] Half-wave potentials, unless otherwise noted. [b] In acetonitrile solution with TEAPF$_6$ as supporting electrolyte. [c] Chemically irreversibile process, E_p value at $v = 0.2$ V s^{-1}. [d] $T = 228$ K. [e] In dimethylformamide solution with TBAPF$_6$ as supporting electrolyte. [f] $T = 219$ K.

PD-NB dyad

Nitrobenzene shows a moderately intense absorption band with $\lambda_{max} = 260$ nm in acetonitrile, no emission band, and a monoelectronic reversible reduction process at −1.08 V in dimethylformamide.[15]

The absorption spectrum of the PD-NB dyad [Fig. 2(a)] is quite similar to the sum of the spectra of the two components. The fluorescence band of the PD unit, however, is completely quenched at 298 K, whereas it is present in rigid matrix at 77 K (Table 1). The CV curve of the dyad in acetonitrile–TBAPF$_6$ solution [Fig. 2(b)] shows the oxidation process of the dansyl moiety ($E_{pa} = +0.92$ V) and the monoelectronic reversible reduction process at −1.10 V of the nitrobenzene unit (Table 2).

Since the nitrobenzene moiety does not possess energy levels below the fluorescent excited state of dansyl, the quenching of the PD fluorescence observed at 298 K cannot be due to energy transfer. By using the observed potential values and eqn. (2), oxidative electron transfer of the fluorescent excited state of PD results to be exoergonic by *ca.* 0.9 eV and it can thus account for the observed quenching [Fig. 2(c)]. Interestingly, the quenching process does not occur in a butyronitrile rigid matrix, presumably because the lack of solvent repolarization prevents stabilization of the electron transfer products.[17] This is confirmed by the fact that in the low polar cyclohexane solvent the fluorescence quenching is negligible even at 298 K.

PD-NA dyad

Naphthalene shows $\pi\pi^*$ absorption bands below 320 nm and a very intense fluorescence with $\lambda_{max} = 336$ nm in acetonitrile solution ($E_{00} = 4.0$ eV),[15] an oxidation process at +1.54 V in acetonitrile,[15] and a reduction process at −2.49 V in dimethylformamide.[15]

The absorption spectrum of the PD-NA dyad [Fig. 3(a)] is quite similar to the sum of the spectra of the dansyl and naphthalene components. The fluorescence band of the naphthalene moiety is not present, whereas the fluorescence of the dansyl moiety is unaffected. The CV curve of the dyad [Fig. 3(b)] shows only the dansyl oxidation peak. The oxidation and reduction peaks of the naphthalene moiety cannot be observed because they are outside the accessible potential window in our experimental conditions. On the reasonable assumption that the excited state energy and the electrochemical properties of the NA component of the PD-NA dyad are the same as those of naphthalene, eqn. (1) shows that energy transfer from the

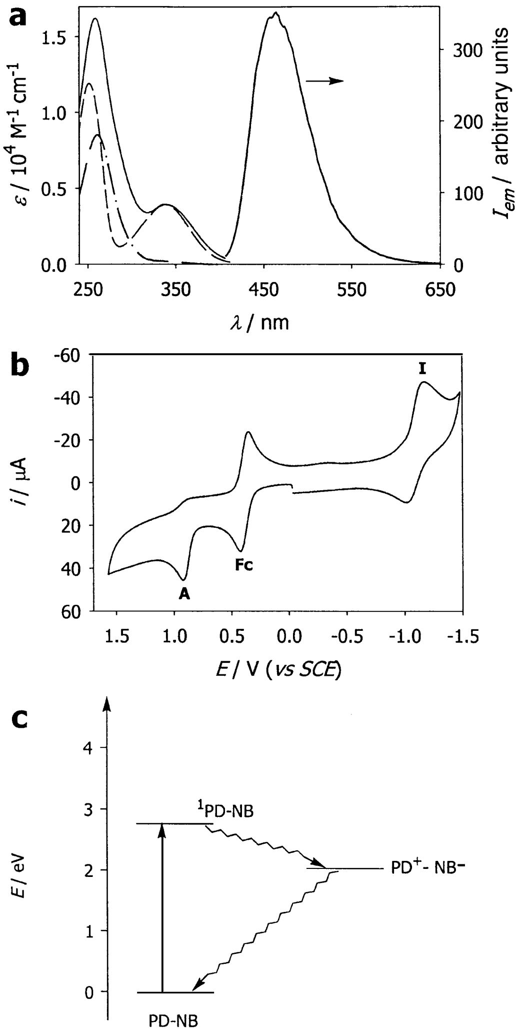


Fig. 2 (a) Absorption (298 K) and emission (77 K) spectra of the PD-NB dyad (full line) and absorption spectra of the PD (dashed line) and nitrobenzene (dashed-dotted line) components in acetonitrile. (b) Cyclic voltammogram of the PD-NB dyad in acetonitrile–TEAPF$_6$ solution. (c) Energy level diagram for the PD-NB dyad in acetonitrile solution at room temperature.

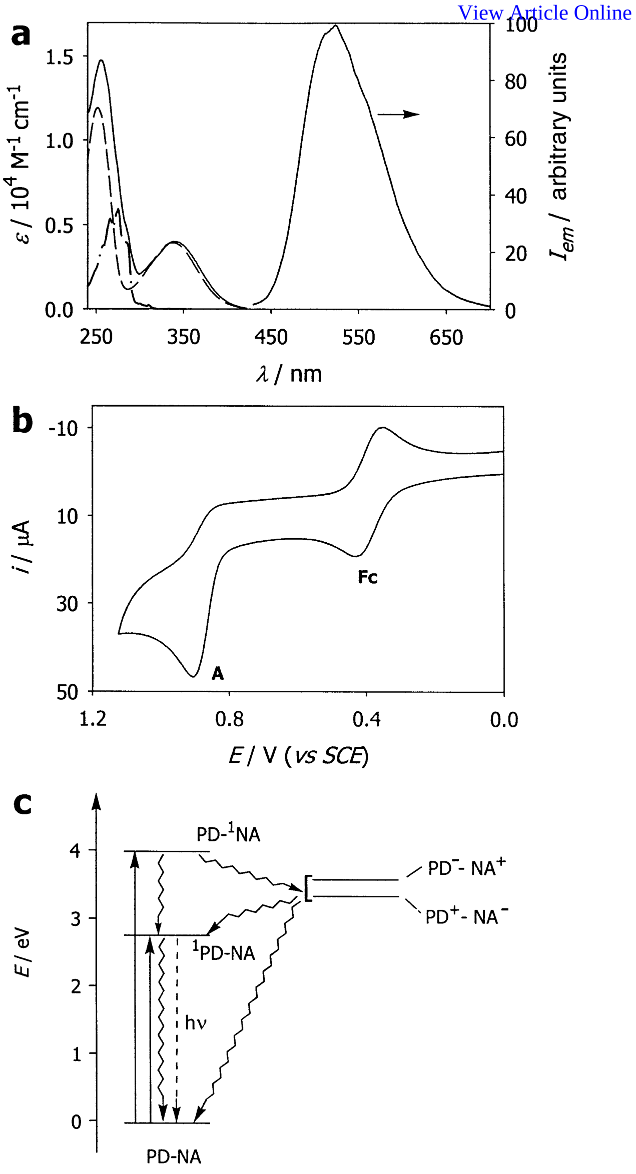


Fig. 3 (a) Absorption and emission spectra of the PD-NA dyad (full line) and absorption spectra of the PD (dashed line) and naphthalene (dashed-dotted line) components in acetonitrile. (b) Cyclic voltammogram of the PD-NA dyad in acetonitrile–TEAPF$_6$ solution. (c) Energy level diagram for the PD-NA dyad.

fluorescent excited state of the NA moiety to that of the PD moiety is exoergonic (ΔG *ca.* − 1.2 eV), and eqn. (2) and (3) show that both the oxidative and reductive electron transfer quenching of the fluorescent excited state of NA by the PD unit are also allowed [ΔG *ca.* − 0.4 and − 0.6 eV, respectively, Fig. 3(c)].

The excitation spectrum of the dyad shows that the light absorbed by the NA component leads to the fluorescence of the PD moiety with 80% efficiency. This result suggests that the quenching of the fluorescent excited state of the naphthalene unit by singlet–singlet energy transfer (which is expected to be very fast *via* a Förster mechanism because of the strong overlap between the naphthalene emission and the dansyl absorption bands) competes efficiently with electron transfer quenching. An alternative explanation for the observed PD fluorescence sensitization is that quenching takes place only by electron transfer and recombination of the ion-pair product leads to the fluorescent excited state of the dansyl moiety [Fig. 3(c)].

PD-*t*AZ and PD-*c*AZ dyads

The *trans* and *cis* isomers of methylazobenzene (*t*MeAZ and *c*MeAZ) were chosen as model compounds for the *t*AZ and *c*AZ units of the PD-*t*AZ and PD-*c*AZ dyads. *t*MeAZ exhibits a very intense $\pi \rightarrow \pi^*$ absorption band with $\lambda_{max} = 325$ nm ($\varepsilon = 23\,400$ cm^{-1} M^{-1}) and a less intense $n \rightarrow \pi^*$ absorption band with $\lambda_{max} = 440$ nm ($\varepsilon = 630$ cm^{-1} M^{-1}). It does not show any emission band, and it undergoes a *trans* → *cis* photoisomerization with $\Phi = 0.20$ and 0.24 at 313 and 365 nm, respectively.

c MeAZ shows absorption bands at $\lambda_{max} = 283$ nm ($\varepsilon = 4950$ cm^{-1} M^{-1}) and $\lambda_{max} = 433$ nm ($\varepsilon = 1500$ cm^{-1} M^{-1}),[18] does not exhibit any emission band, and undergoes a *cis* → *trans* photoisomerization with $\Phi = 0.73$ at 435 nm.

The absorption spectrum of the PD-*t*AZ dyad [Fig. 4(a)] is that expected from the sum of the spectra of the PD and *t*MeAZ components. The emission band of the PD unit with $\lambda_{max} = 510$ nm is completely quenched, and light excitation causes the *trans* → *cis* photoisomerization with $\Phi = 0.15$ at 313 nm (where 15% of the light is absorbed by the dansyl unit) and 0.11 at 365 nm (where 50% of the light is absorbed by the dansyl unit). Comparison of these results with those obtained with the PD and *t*MeAZ model compounds (Table 1) shows that the fluorescent excited state of the PD unit is quenched by the *t*AZ moiety, and suggests that the light absorbed by the PD unit is not effective (within the uncertainties due to the large experimental error) for the *t*AZ photoisomerization reaction.

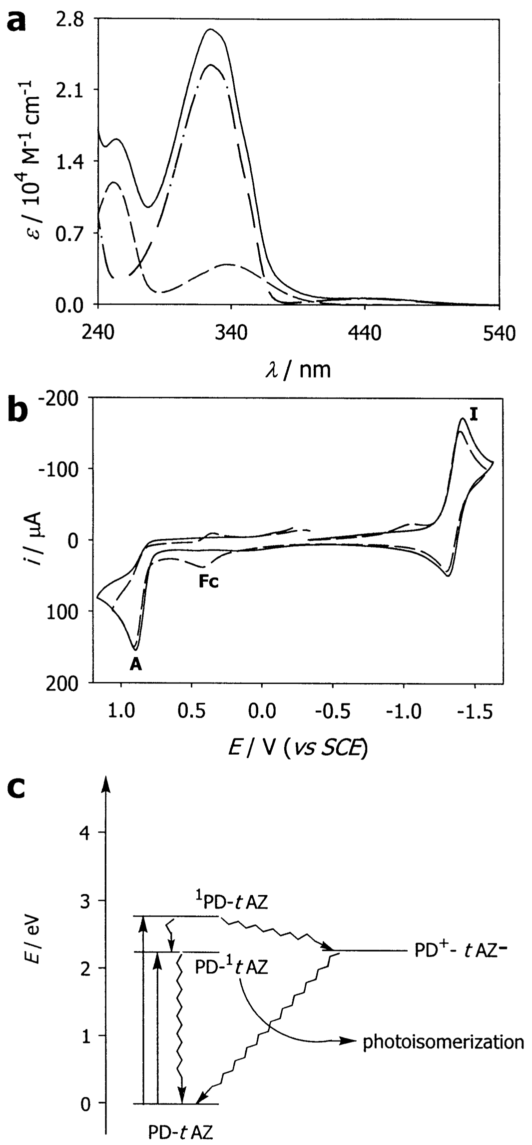


Fig. 4 (a) Absorption spectra of the PD-*t*AZ dyad (full line) and the PD (dashed line) and *t*MeAZ (dashed-dotted line) components in acetonitrile. (b) Cyclic voltammogram of the PD-*t*AZ (full line) and PD-*c*AZ (dashed line) dyads in acetonitrile–TEAPF$_6$ solution. (c) Energy level diagram for the PD-*t*AZ dyad.

The CV curve for the PD-*t*AZ dyad [Fig. 4(b)] shows the oxidation peak of the PD moiety and a reversible reduction peak at -1.35 V, assigned to the *t*AZ unit. It follows that the quenching of the fluorescent excited state of the PD moiety by the *t*AZ moiety *via* an oxidative electron transfer process [eqn. (2)] is exoergonic [ΔG *ca.* -0.5 eV, Fig. 4(c)]. Therefore, the lack of PD sensitization of the *t*AZ isomerization could be explained by the occurrence of an electron transfer quenching process faster than energy transfer. A more extensive study of this system, however, has revealed other interesting aspects.

It is well known that the *cis*-azobenzene species obtained by irradiation of the *trans* isomers undergo a back *cis* → *trans* photoisomerization reaction (which also occurs, slowly, in the dark).[19] Therefore, continuous irradiation of a *trans* (or *cis*) azobenzene species leads to a photostationary state in which the concentrations of the two isomers depend on the photoisomerization quantum yields and molar absorption coefficients at the excitation wavelength and the rate of back *cis* → *trans* isomerization:

$$[\mathrm{t}]/[\mathrm{c}] = \Phi_{\mathrm{c}->\mathrm{t}}\,\varepsilon_{\mathrm{c}}/(\Phi_{\mathrm{t}->\mathrm{c}}\,\varepsilon_{\mathrm{t}}) \qquad (4)$$

In practice, since the quantum yield values are not strongly dependent on the excitation wavelength,[19] the molar fractions of the two isomers in the photostationary state on changing excitation wavelength roughly parallel the large changes observed in the ratio of the molar absorption coefficients of the two isomers.

In the case of MeAZ, the molar fraction of *trans* isomer present at the photostationary state depends on the excitation wavelength (85% at 435 nm, 5% at 365 nm, and 28% at 313 nm) roughly as expected on the basis of the fraction of light absorbed by each isomer at the different excitation wavelengths. For the PD-*t*AZ dyad, the photostationary state contains approximately the same molar fraction of *trans* isomer (*ca.* 90%) as in the case of MeAZ when excitation is performed at 435 nm, where the PD moiety does not absorb; however, the molar fraction of *trans* isomer is much larger at 365 (69%) and 313 nm (43%), where the light absorbed by the PD unit is 50 and 15%, respectively. It can also be noted that the molar fraction of *trans* isomer at the photostationary state for the dyad is larger at 365 than at 313 nm, even if the ratio between the molar absorption coefficients of the *trans* and *cis* isomers is 29 at 365 nm and 9 at 313 nm. These results force us to conclude that in the dyad the light absorbed by the PD moiety is ineffective (or almost so) for the *trans* → *cis* isomerization, but it does sensitize the reverse *cis* → *trans* process. From a quantitative viewpoint, we have estimated that the molar fraction of *trans* isomer at the photostationary state upon 313 or 365 nm excitation in the PD-*c*AZ dyad is close to that expected in the case of an energy transfer process with unitary efficiency from the PD to the *c*AZ moiety.[20]

Since the redox properties of the *trans* and *cis* isomers are practically identical (Table 2), it seems unlikely that the quenching of the fluorescence of the PD moiety occurs by electron transfer in the PD-*t*AZ dyad and by energy transfer in the PD-*c*AZ one. An alternative, and more likely, explanation is that energy transfer takes place in both PD-*t*AZ and PD-*c*AZ, but, because of the shape of the excited state potential energy curve, it leads to excited state geometries that can only deactivate to the *trans* isomer. The theoretical interpretation of the direct and sensitized photoisomerization of azobenzene has been the object of much debate.[19,21] A description of the phenomenon is even more difficult for our dyads since the PD moiety can affect the isomerization process by electronic perturbation as well as by steric constraints.

PD-BPY dyad

The absorption spectrum of the PD-BPY dyad [Fig. 5(a)] is quite similar to the sum of the spectra of the PD and 2,2′-bipyridine components. The electrochemical behavior of this dyad was studied in dimethylformamide solution since it is known that 2,2′-bipyridine exhibits a reduction process in a cathodic region that cannot be explored in acetonitrile. The CV curve of the PD-BPY dyad in dimethylformamide [Fig. 5(b)] shows the dansyl oxidation peak and a reduction process at *ca.* -2.0 V (Table 2), overlapping the solvent discharge. At 219 K the potential window is wider, and it becomes possible to see that the reduction process is reversible ($E_{1/2} = -2.03$ V). Such a process occurs at a potential very close to that exhibited by free BPY in dimethylformamide (-2.01 V). On the basis of the electrochemical results, the energy of the PD-to-BPY electron transfer level is around 2.9 eV. This value is smaller than the energy of the singlet excited state of the BPY unit (*ca.* 4.0 eV),[22] but higher than the energy (2.8 eV) of the fluorescent excited state of the PD unit [Fig. 5(c)].

2,2′-Bipyridine and its derivatives are weakly or not at all fluorescent in fluid solution at 298 K.[22] In the emission spectrum of the dyad [Fig. 5(a)], only the dansyl fluorescence band is observed, both in fluid solution at 298 K and in rigid glasses

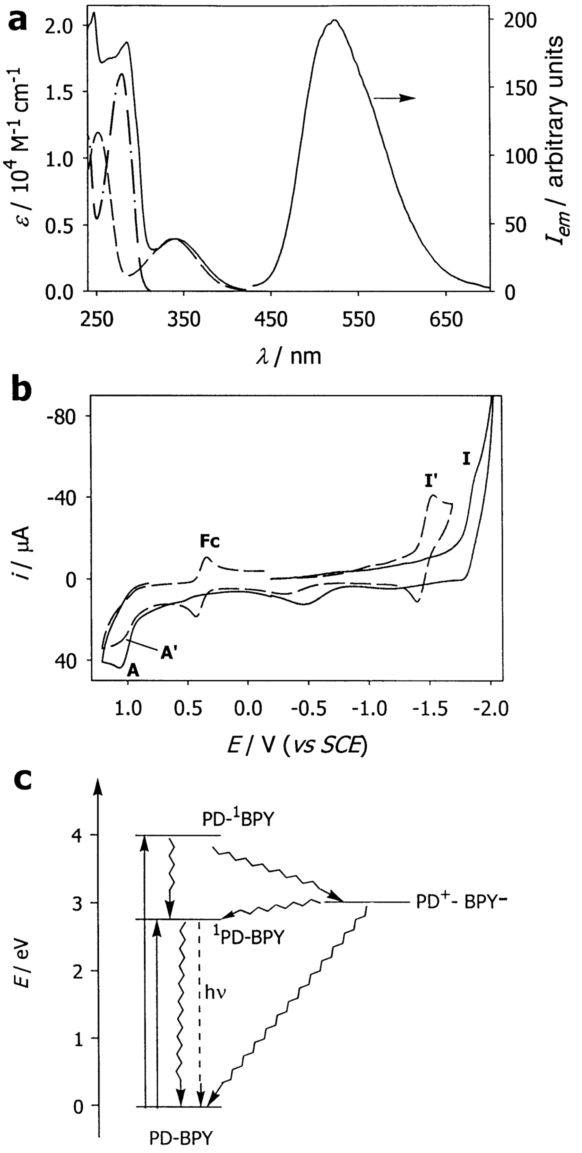


Fig. 5 (a) Absorption and emission spectra of the PD-BPY dyad (full line) and absorption spectra of the PD (dashed line) and 2,2′-bipyridine (dashed-dotted line) components in acetonitrile. (b) Cyclic voltammogram of the PD-BPY dyad before (full line) and after (dashed line) addition of 5 equiv. of $Zn(NO_3)_2$ in dimethylformamide–$TBAPF_6$ solution. (c) Energy level diagram for the PD-BPY dyad.

at 77 K. The excitation spectrum shows that energy transfer from the BPY excited states to the fluorescent level of the dansyl unit is at least 80% efficient. Therefore, either the Förster-type energy transfer process is faster than electron transfer, or recombination of the ion-pair obtained by electron transfer leads to the fluorescent excited state of the dansyl moiety [Fig. 5(c)].

PD-BPY(Zn^{2+}) and PD-BPY(H^+) dyads. Since it is known that BPY can coordinate metal ions and protons, we have studied the effect of Zn^{2+} and H^+ on the spectroscopic and electrochemical properties of the PD-BPY dyad.

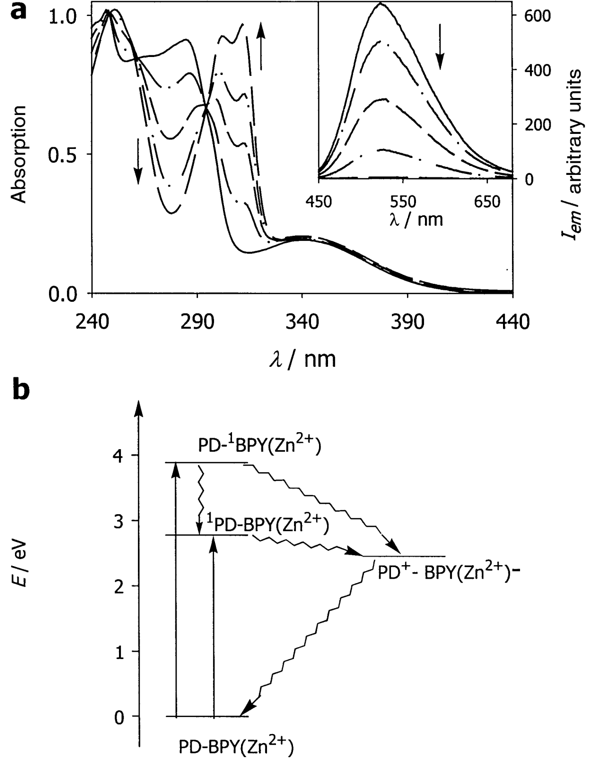


Fig. 6 (a) Absorption and emission (inset) spectral changes observed upon addition of Zn^{2+} (0, 0.1, 0.2, 0.3, 0.5, 5 equiv.) to an acetonitrile solution of the PD-BPY dyad. (b) Energy level diagram for the PD-BPY(Zn^{2+}) dyad.

Upon addition of Zn^{2+} to a solution of the PD-BPY dyad, strong changes were observed in the absorption and emission spectra [Fig. 6(a)]. The absorption band of the dansyl moiety ($\lambda_{max} = 340$ nm) was unchanged, whereas the disappearance of the uncoordinated BPY absorption band ($\lambda_{max} = 285$ nm) was accompanied by the appearance of a new band at 310 nm and the disappearance of the dansyl emission ($\lambda_{max} = 510$ nm). The presence of isosbestic points indicates that only one complex species is formed. A plateau was reached after addition of 5 equiv. of Zn^{2+}. The observed spectral changes are assigned to the formation of the PD-BPY(Zn^{2+}) dyad.

CV experiments on the PD-BPY dyad in dimethylformamide solution containing 5 equiv. Zn^{2+} showed that the process occurring at the edge of solvent discharge (*vide supra*) was no longer observed, and a new reduction process was present at -1.43 V, assigned to the PD-BPY(Zn^{2+}) species [Fig. 5(b)]. In such a dyad, the energy of the PD-to-BPY(Zn^{2+}) electron transfer level should be around 2.3 eV, lower than the energy of the fluorescent excited state of the dansyl unit [Fig. 6(b)], thereby accounting for the observed quenching of the PD fluorescence. In butyronitrile rigid matrix at 77 K, however, no fluorescence quenching was observed, showing again that the energy of the electron transfer level raises above the energy of the fluorescent level of the dansyl moiety.

Upon addition of trifluoroacetic acid to acetonitrile solutions of PD-BPY, absorbance changes were first observed only in the spectral region below 320 nm, whereas the dansyl absorption band with $\lambda_{max} = 340$ nm was practically unaffected. This result shows that protonation first occurs at the BPY moiety, in agreement with the reported pK_a of BPY and dansyl containing compounds in water.[23] The titration reaction takes place with maintenance of the isosbestic points, is fully reversible, and reaches a plateau after addition of 20 equiv. of acid. The changes in absorbance of the BPY centered band are accompanied by a parallel decrease in the intensity of the dansyl fluorescence. This finding shows that protonated BPY quenches the dansyl fluorescence. Since protonated BPY does not possess excited states below the fluorescent excited state of the dansyl unit, the observed quenching is likely due to an electron transfer process. The actual reduction potential of protonated BPY cannot be measured because the presence of an excess of trifluoroacetic acid limits the potential window that can be investigated.

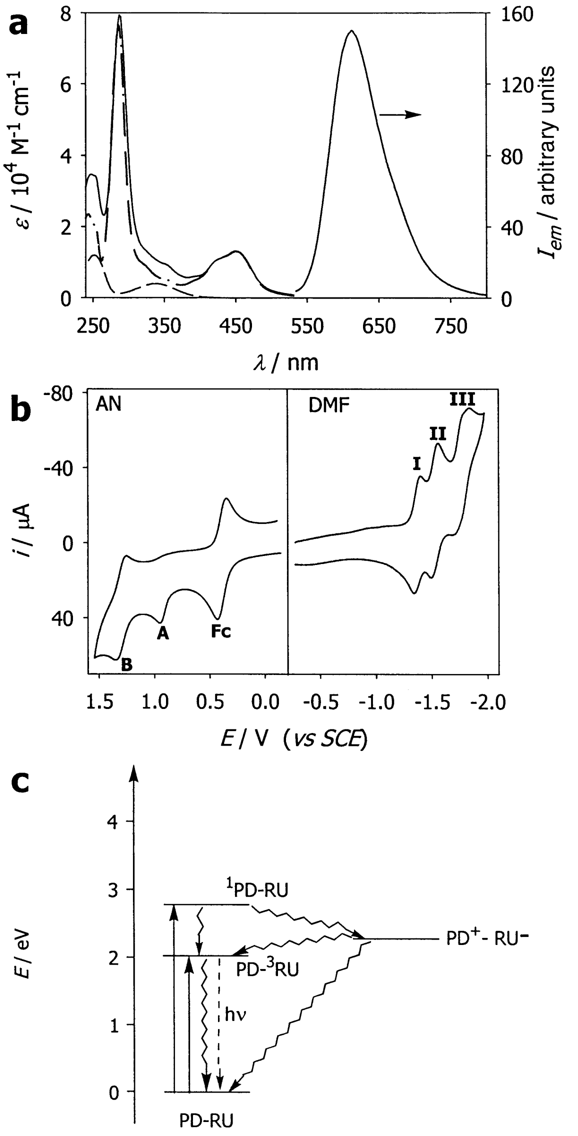


Fig. 7 (a) Absorption and emission spectra of the PD-RU dyad (full line) and absorption spectra of the PD (dashed line) and $[Ru(bpy)_3]^{2+}$ (dashed-dotted line) components in acetonitrile. (b) Cyclic voltammogram of the PD-RU dyad in acetonitrile–$TBAPF_6$ (anodic region) and dimethylformamide–$TBAPF_6$ (cathodic region) solutions. (c) Energy level diagram for the PD-RU dyad in acetonitrile solution at room temperature.

Upon further addition of acid, the dansyl absorption band gradually disappears, as expected upon protonation of the dansyl amine moiety.[7a]

PD-RU dyad

The absorption spectrum of the PD-RU dyad [Fig. 7(a)] is that expected from the sum of the spectra of the dansyl and $[Ru(bpy)_3]^{2+}$ components.[24] As can be seen, the absorption of the $[Ru(bpy)_3]^{2+}$ moiety is by far the predominant one in most of the spectral region. In the emission spectrum of the dyad the band of the dansyl unit is quenched by at least 100 times compared to that of the free PD unit. The characteristic band of $[Ru(bpy)_3]^{2+}$ ($\lambda_{max} = 620$ nm, $\Phi = 0.013$, $\tau = 176$ ns) is practically unaffected by the PD moiety. The excitation spectrum in the region between 300 and 400 nm, where the contribution of the dansyl absorption is relatively large [Fig. 7(a)], does not coincide with the absorption spectrum, suggesting that a substantial fraction of the quenching of the dansyl fluorescence is not due to energy transfer to the $[Ru(bpy)_3]^{2+}$ moiety. Careful comparison between the emission intensities of isoabsorptive $[Ru(bpy)_3]^{2+}$ and PD-RU solutions at 340 nm (where in the dyad 40% of the light is absorbed by the PD unit) and 470 nm (where the light is only absorbed by the $[Ru(bpy)_3]^{2+}$ moiety) has shown that only 25% of the quenching of the dansyl fluorescence is due to energy transfer.

The CV curve of the dyad [Fig. 7(b)] shows the characteristic dansyl anodic peak at +0.96 V and a reversible one-electron process with $E_{1/2} = +1.31$ V, assigned to the oxidation of the $[Ru(bpy)_3]^{2+}$ unit.[24] On the cathodic side, the three expected reduction processes of the $[Ru(bpy)_3]^{2+}$ unit[24] are observed. Since the first reduction takes place at −1.30 V, the energy of the PD-to-RU electron transfer process is approximately 2.2 eV, so that electron transfer quenching of the fluorescent excited state of the dansyl unit (2.8 eV) is thermodynamically allowed [Fig. 7(c)] and can account for the large fraction (75%) of the quenching of the dansyl excited state that is not due to energy transfer. The formation of the triplet excited state of the $[Ru(bpy)_3]^{2+}$ moiety on excitation of the PD unit *via* forward and back electron transfer cannot be excluded. A summary of the processes taking place upon excitation of the PD-RU dyad is shown schematically in Fig. 7(c).

Conclusions

In order to elucidate the excited state behavior of the dansyl chromophoric group, which is extensively used for labelling purposes in supramolecular systems and dendrimers,[6,7,25] we have studied the photochemical, photophysical and electrochemical properties of six novel dyads (Scheme 1) made of a propyldansylamide (PD) unit covalently linked to nitrobenzene (NB), naphthalene (NA), *trans*- and *cis*-azobenzene (*t*AZ and *c*AZ), 2,2′-bipyridine (BPY), and $[Ru(bpy)_3]^{2+}$ (RU) moieties. Because of the great diversity of the units linked to the common dansyl chromophoric group, a variety of processes have been observed, such as sensitization of the dansyl fluorescence, quenching of the dansyl fluorescence by electron or energy transfer, and sensitized emission and reaction of the other component of the dyad. The results of this systematic investigation will be useful for the design of new supramolecular sensors, switching elements, and photoactive dendrimers.

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