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Stereoselective fluorescence quenching by photoinduced electron transfer in naphthalene-amine dyads

Uwe Pischel,*[ab] Sergio Abad[a] and Miguel A. Miranda*[a]

[a] *Instituto de Tecnología Química, Universidad Politécnica de Valencia, UPV-CSIC, Av. de los Naranjos s/n, E-46022 Valencia, Spain. E-mail: mmiranda@qim.upv.es; Fax: +34 96 387 78 09; Tel: +34 96 387 78 07*

[b] *CEQUP/Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal*

Received (in Cambridge, UK) 13th February 2003, Accepted 12th March 2003
First published as an Advance Article on the web 2nd April 2003

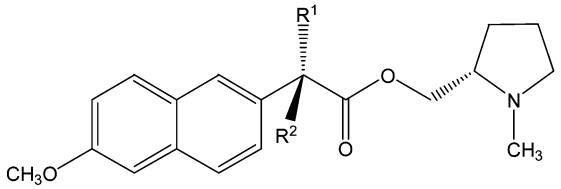
Intramolecular chiral recognition in electron-transfer-induced fluorescence quenching has been observed for diastereomeric dyads composed of a naphthalene chromophore and an amine.

The interaction of singlet-excited aromatics with electron-donating amines provides a classical example of photoinduced electron transfer reactions.[1,2] Several aspects of this photoreaction including the influence of factors like solvent polarity,[3] electronic structure of the electron donor,[4] and singlet-excited state energy are connected with the driving force of electron transfer by the well-known Rehm-Weller equation:

$$\Delta G_{et} = E_{ox}(D) - E_{red}(A) - E^* + C.$$

Less straightforwardly predictable is the influence of geometrical parameters. Irie and co-workers investigated the *intermolecular* quenching of (*R*)-(−)-1,1′-binaphthyl by chiral benzylamines.[5] In nonpolar solvents a stereoselective photophysics was observed. However, in acetonitrile no stereodifferentiation was noted. The authors argued that in polar media electron transfer becomes dominant, while in nonpolar solvents exciplex formation is the major quenching pathway. The latter is more subjected to geometrical influences due to a closer interaction in form of an orbital overlap between donor and acceptor. Other related work included binaphthol and its derivatives, whose fluorescence was quenched by chiral amines.[6] This led to their application as chiral chemosensors.[7]

In order to investigate chiral discrimination in electron-transfer induced *intramolecular* quenching, we have synthesized two dyads from the enantiomers of a naphthalene derivative, i.e., (*S*)-(+)- and (*R*)-(−)-6-methoxy-2-naphthylpropionic acid (naproxen, NPX), and *N*-methyl-(*S*)-pyrrolidinemethanol (PYR). The synthesis was realised by conversion of (*R*)- or (*S*)-naproxen with thionyl chloride into the activated acyl chloride and esterification of the latter with the hydroxyl-functionalised pyrrolidine derivative in dichloromethane. Both compounds were purified by preparative reverse-phase HPLC with acetonitrile as eluent. Their identity was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy.†



$R^1 = CH_3$; $R^2 = H$ (S,S)-NPX-PYR

$R^1 = H$; $R^2 = CH_3$ (R,S)-NPX-PYR

The absorption spectra of both diastereomers show two fine-structured bands with maxima at λ_{max} = 273 nm and 332 nm, akin to the parent naproxen.[8] These absorptions are ascribed to π,π*-type transitions. Noteworthy, the π,π*-transitions of the diastereomers compared to naproxen are not altered, neither in oscillator strength nor spectral position. This indicates the absence of significant ground-state interaction between the naphthalene chromophore and the amine.

The fluorescence spectra of (*S*,*S*)-NPX-PYR, (*R*,*S*)-NPX-PYR, and (*S*)-naproxen in acetonitrile are characterised by a typical emission band centred at 350 nm (Figure 1).[8] The excitation spectra present the same bands as the absorption spectra, which unambiguously confirms the origin of the emission as coming from the naphthalene residue. Steady-state fluorescence measurements upon excitation at 280 nm of optically matched (A = 0.2) aerated acetonitrile solutions of NPX-PYR diastereomers revealed a fluorescence quenching for both compounds in comparison to parent naproxen (Figure 2). The generally accepted quenching mechanism in such systems is photoinduced electron transfer from the amine to the aromatic residue. The thermodynamics for this process can be calculated with the mentioned Rehm-Weller equation using: E_{ox} = +0.96 V *vs.* SCE for triethylamine,[9] E_{red} = −2.60 V *vs.* SCE for 2-methoxynaphthalene,[10] E^* = 3.69 eV for naproxen,[8] and C = −0.06 eV for the coulombic term. An exergonic driving force of

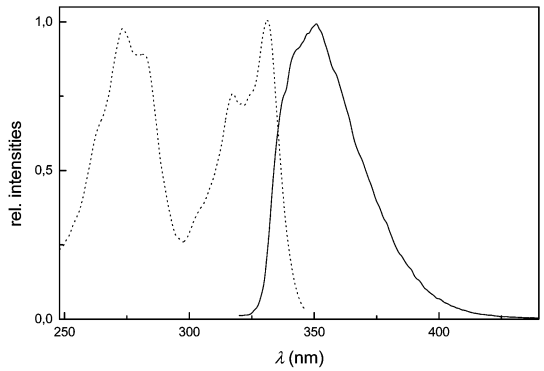


Fig. 1 Normalised fluorescence emission (solid line) and excitation (dotted line) spectra of (*S*,*S*)-NPX-PYR in aerated acetonitrile.

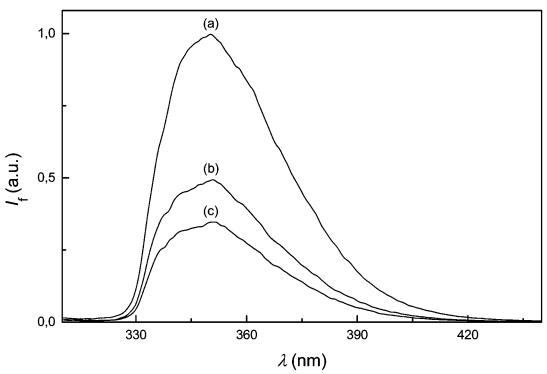


Fig. 2 Fluorescence emission spectra (λ_{exc} = 280 nm) of optically matched solutions of (a) (*S*)-naproxen, (b) (*S*,*S*)-NPX-PYR, and (c) (*R*,*S*)-NPX-PYR in aerated acetonitrile.

DOI: 10.1039/b301414b

$\Delta G_{et} = -0.19$ eV results. Notably, at the chosen concentration of *ca.* 5×10^{-5} M the contribution of *intermolecular* quenching is less than 1% [with $k_q = 5.1 \times 10^9$ $M^{-1}s^{-1}$ for the naphthalene/triethylamine system in acetonitrile[11] and $\tau_0 = 7.44$ ns for (*S*)-naproxen in aerated acetonitrile].

Most strikingly, the amount of quenching, i.e., the quantum yield of electron transfer Φ_{et}, for the two diastereomers is significantly different, which must be related to a stereoselective electron transfer. Here the (*S*,*S*)-diastereomer shows a lower efficiency than the (*R*,*S*) combination, i.e, $\Phi_{et} = 0.52$ *versus* 0.66. The same trend is observed for the fluorescence lifetime of the naphthalene chromophore, which was determined by time-correlated single-photon-counting measurements (Figure 3). (*S*)-Naproxen itself has a lifetime of 7.44 ns in aerated acetonitrile solution, while the lifetimes τ_f of (*S*,*S*)-NPX-PYR and (*R*,*S*)-NPX-PYR are 3.02 ns and 2.35 ns, respectively. Quantum yields for electron transfer can also be derived from these data, i.e., 0.59 and 0.68 for (*S*,*S*)- and (*R*,*S*)-NPX-PYR, respectively. Hence, the unimolecular rate constant for electron transfer can be calculated with $k_{et} = \Phi_{et}/\tau_f$. The following values result: k_{et} (*S*,*S*) $= 1.8 \times 10^8$ s^{-1} and k_{et} (*R*,*S*) $= 2.8 \times 10^8$ s^{-1} indicating a factor of *ca.* 1.6 for the stereodifferentiation between both diastereomers.

In order to support the proposed electron transfer mechanism the experiment was performed in a less polar solvent, i.e., *n*-hexane. However, no significant fluorescence quenching was observed in the case of the dyads and therefore no stereodifferentiation. Obviously, the thermodynamics disfavours electron transfer to a high extent as a consequence of the destabilisation of the intramolecularly formed radical ion pair. This serves as corroboration of photoinduced electron transfer in the present dyads. However, a closer inspection of the fluorescence spectra in acetonitrile revealed a very small but significant red-shifted broad emission band with a maximum at *ca.* 540–550 nm. It can be ascribed to an exciplex emission in analogy to the observations made for 2-naphthylmethylamine.[12] The excitation spectrum according to this emission matches the absorption spectrum of the dyad, which confirms the origin of this fluorescence. A comparison of the emission intensities of the monomer (at 350 nm), i.e., the naphthalene chromophore, and the exciplex (at 550 nm) reveals ratios of $I_{monomer}/I_{exciplex} = 90$ and 40 for (*S*,*S*)-NPX-PYR and (*R*,*S*)-NPX-PYR, respectively. This can be identified as minor compared to 2-naphthylmethylamine, where the exciplex emission in acetonitrile is *ca.* 4 times more intense than the naphthalene fluorescence.[12] Therefore, formation of exciplexes is a minor pathway compared to full electron transfer for the investigated systems.

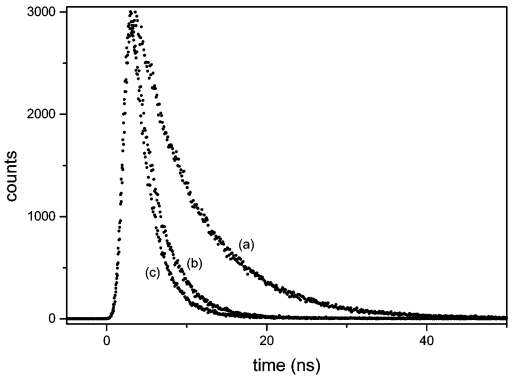


Fig. 3 Fluorescence decay traces ($\lambda_{exc} = 280$ nm, $\lambda_{obs} = 350$ nm) of (a) (*S*)-naproxen, (b) (*S*,*S*)-NPX-PYR, and (c) (*R*,*S*)-NPX-PYR in aerated acetonitrile.

The reason for sensitivity of the electron transfer rate to the chiral information in the present system must be sought in the steric hindrance associated with the necessary approach of donor and acceptor moiety.[13] As the reaction is only moderately exergonic, such steric effect could have a strong impact on the actual height of the activation barrier. Finally, in an *intermolecular* control experiment (*S*)- and (*R*)-naproxen fluorescence was quenched by the acetyl ester of *N*-methyl-(*S*)-pyrrolidinemethanol in acetonitrile. The rate constants are with 1.2 and 1.0×10^{10} $M^{-1}s^{-1}$, respectively, close to diffusion control. Therefore the enantioselectivity factor is strongly reduced (*cf.* reactivity–selectivity principle). However, in this case the (*S*)/(*S*) combination showed a slightly higher reactivity, opposite to the *intramolecular* experiment.

The presented results suggest that exciplex formation is not always a precondition for the observation of stereodifferentiation in charge transfer processes.[14]

The financial support by MCYT (Grant No. BQU2001-2725) and the Deutsche Forschungsgemeinschaft (Research Fellowship for U.P.) is gratefully acknowledged.

Notes and references

† **(*S*,*S*)-NPX-PYR**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 1.40–1.52 (1H, m, CH_2 PYR), 1.58 (3H, d, $J = 7.2$ Hz, CH_3), 1.60–1.85 (3H, m, CH_2 PYR), 2.12–2.22 (1H, m, CH_2 PYR), 2.29 (3H, s, CH_3N) 2.33–2.43 (1H, m, CH_2 PYR), 2.96–3.03 (1H, m, CH PYR), 3.88 (1H, q, $J = 7.2$ Hz, CH), 3.91 (3H, s, CH_3O), 3.99–4.11 (2H, m, CH_2), 7.09–7.16 (2H, m, arom. CH), 7.40 (1H, dd, $J = 8.5$ and 1.9 Hz, arom. CH), 7.66–7.71 (3H, m, arom. CH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 18.4 (CH_3), 22.8 (CH_2 PYR), 28.3 (CH_2 PYR), 41.3 (CH_3N), 45.4 (CH), 55.3 (CH_3O), 57.6 (CH_2 PYR), 63.7 (CH PYR), 67.1 (CH_2), 105.6, 118.9, 126.0, 126.3, 127.0 (arom. CH), 128.9 (arom. C), 129.3 (arom. CH), 133.7, 135.7, 157.6 (arom. C), 174.7 (CO).

(*R*,*S*)-NPX-PYR: ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 1.40–1.53 (1H, m, CH_2 PYR), 1.58 (3H, d, $J = 7.2$ Hz, CH_3), 1.62–1.90 (3H, m, CH_2 PYR), 2.07–2.12 (1H, m, CH_2 PYR), 2.28 (3H, s, CH_3N) 2.33–2.43 (1H, m, CH_2 PYR), 2.94–3.02 (1H, m, CH PYR), 3.87 (1H, q, $J = 7.2$ Hz, CH), 3.91 (3H, s, CH_3O), 4.04–4.08 (2H, m, CH_2), 7.09–7.16 (2H, m, arom. CH), 7.40 (1H, dd, $J = 8.5$ and 1.9 Hz, arom. CH), 7.65–7.71 (3H, m, arom. CH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 18.5 (CH_3), 22.8 (CH_2 PYR), 28.5 (CH_2 PYR), 41.5 (CH_3N), 45.5 (CH), 55.3 (CH_3O), 57.6 (CH_2 PYR), 63.8 (CH PYR), 67.5 (CH_2), 105.6, 118.9, 126.0, 126.4, 127.1(arom. CH), 128.9 (arom. C), 129.3 (arom. CH), 133.7, 135.7, 157.6 (arom. C), 174.6 (CO).

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