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Organic Electronics 5 (2004) 129–134

Organic Electronics

www.elsevier.com/locate/orgel

Effects of intermolecular interactions on photoluminescence efficiency of crystalline thienylene-*S*,*S*-dioxide molecular semiconductors

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Received 6 June 2003; received in revised form 18 October 2003; accepted 18 November 2003
Available online 7 December 2003

Abstract

The effects of intermolecular interactions on the photoluminescence (PL) quantum efficiency of differently substituted thienylene-*S*,*S*-dioxide derivatives in the crystalline phase are investigated. The exciton resonance interactions and the transfer integrals are evaluated using a quantum chemistry approach by considering the supramolecular structures obtained from X-ray data. Two classes of thienylene-*S*,*S*-dioxides are investigated: (1) rigid, fused ring compounds, for which the PL quantum efficiency can be well correlated with the rate of formation of non-radiatively decaying charge-transfer pairs upon photoexcitation; (2) flexible oligothiophenes for which the high PL quantum efficiency in the solid-state is assigned to a decrease of intramolecular internal conversion process, as confirmed by time-resolved PL measurements in solvents of different viscosity.

Keywords: Photoluminescence; Interchain interactions; Quantum yield; Viscosity; Polythiophenes and derivatives

1. Introduction

In the context of organic molecular semiconductors, thiophene derivatives are relevant for the high chemical stability [1], the excellent transport properties [2] and for the wide color tunability [3]. On the other hand they are characterized by low photoluminescence quantum efficiency (PLQE) in the solid-state [4] which limits their use as active materials in light-emitting diodes (LEDs). Recently, chemically modified oligothiophenes in which the central thienyl sulphur atom is functionalized with two oxygen atoms were used in high efficient LEDs [5,6] and lasers [7]. The class of thienylene-*S*,*S*-dioxides includes *flexible* oligothiophenes [8] with low inter-ring torsional barriers and *rigid* dithienothiophenes [9] with fused rings. These compounds show high PLQE in the solid-state up to 70% [8] and have electron affinity up to 3

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doi:10.1016/j.orgel.2003.11.002

eV, thus representing an important class of molecular semiconductors for optoelectronic applications.

The origin of the high PLQE in the solid-state is not fully understood. Intermolecular interactions are expected to increase the non-radiative decay rate of excitons due to their migration to quenching sites (defects or impurities), the formation of *H*-aggregates characterized by lower-energy optically forbidden states [10] or the formation of charge-transfer excitons [11]. Thus, the PLQE in the solid-state is, in general, lower than that of isolated molecules in dilute solutions. This general trend is valid for dithienothiophene-*S*,*S*-dioxides [9] but not for flexible oligothiophene-*S*,*S*-dioxides, which show PLQE in solution much lower than in the solid-state [8]. Furthermore in all thienylene-*S*,*S*-dioxides the SO_2 group induces a supramolecular structure different from the herringbone one typical of unsubstituted oligothiophenes [12]. As recently pointed out, an increased PL emission in the solid-state could be due to the formation of radiative *J*-aggregates [13,14]. Moreover, we note that the electronic structure and the photophysics of oligothiophene-*S*,*S*-dioxides are different from unsubstituted oligothiophenes [15]. The main non-radiative channel in oligothiophene-*S*,*S*-dioxides has been assigned to S_1–S_0 internal conversion (IC) [16], whereas in unsubstituted oligothiophenes it has been assigned to inter-system crossing (ISC) [17–19].

The PLQE in molecular crystals is the result of several factors, depending on both the molecular and supramolecular structure. Moreover, the molecular conformation can be modified by the crystal packing, e.g. in the case of conformational polymorphism [19]. A theoretical and semi-quantitative analysis of the photophysical processes in molecular crystals is thus required but it is possible only when X-ray data are available, because of the lack of well established theoretical approaches for predicting the solid-state organization of organic molecules.

In this work we theoretically investigate the role of intermolecular interactions on the PLQE of five differently substituted thienylene-*S*,*S*-dioxide derivatives, for which powder X-ray diffraction data are available [9,12]. The molecules investigated (see Fig. 1) are: dithieno[3,2-b:2′,3′-d]thiophene-4,4-dioxide (DTTox), 3,5-dimethyl-dithieno[3,2-b:2′,3′-d]thiophene-4,4-dioxide (DTToxMe), 3,5-dimethyl-2,3′-bis(3-methylthiophene)-dithieno[3,2-b:′,3′-d]thiophene-4,4-dioxide (ThDTToxMe), 3′,4′-di(hexyl)-2,2′:5′,2″-ter-thiophene-1′,1′-dioxide (T3oxHex), 2,5-bis(phenyl)-3,4-di(hexyl)-thiophene-1,1-dioxide (DPToxHex). We calculate both the exciton resonance interactions and the transfer integrals. The former controls the formation of *J*-/*H*-aggregates, the latter the formation of charge-transfer pairs (see Section 2). Considering the size of the molecules and the presence of up to four molecules in the unitary cell, accurate first-principles calculations [20,21] are computationally too expensive. We here use a semi-emipirical approach.

In order to investigate the effects of the environment on the non-radiative decay rate, we also performed time-resolved PL measurements on a model system, i.e. 2,5-bis(phenyl)-thiophene-1,1-dioxide (DPTox), in solvents of different viscosity.

2. Computational method

We calculated the exciton resonance interaction [22] for each couples of molecules (A, B), along all the directions, using the X-ray structural data:

$$\gamma_{AB} = \iint \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 P_A(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} P_B(\mathbf{r}_2). \tag{1}$$

The transition density $P(\mathbf{r})$ and the two-electron integrals have been calculated within INDO/S (intermediate neglect of differential overlap/spectroscopic parametrization) scheme [23]. The evaluation of the exact resonance interaction overcomes all the limitations of the dipole–dipole approximation [24]

$$\gamma_{AB} \approx \frac{\mathbf{d}_A \cdot \mathbf{d}_B}{R^3} - 3\frac{(\mathbf{d}_A \cdot \mathbf{R})(\mathbf{d}_B \cdot \mathbf{R})}{R^5}, \tag{2}$$

where $\mathbf{d}$ is the molecular transition dipole moment and $\mathbf{R}$ the intermolecular distance.

The role of charge-transfer excitons in photoluminescence quenching has been evaluated by

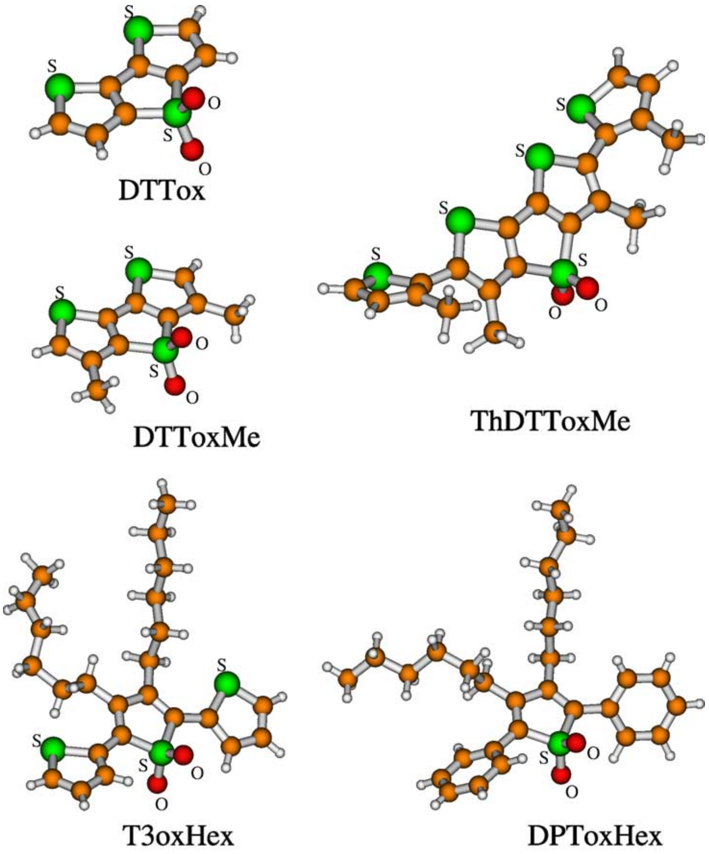

Fig. 1. Chemical structures of the molecules under investigation.

calculating the interchain transfer integrals [25–27] for each molecular pair in the crystal structures. As an estimation of the 'averaged' hole transfer integrals among all directions we calculate

$$t_{\mathrm{h}}^{\mathrm{sum}} = \sum_{B} |\langle \psi^{A}_{\mathrm{HOMO}} | H | \psi^{B}_{\mathrm{HOMO}} \rangle|, \tag{3}$$

where ψ_{HOMO} is the INDO/S wavefunction of the highest occupied molecular orbital (HOMO) of the unperturbed (isolate) molecule. The sum is over all the molecules B in the cluster of molecules around the molecule A and H is the Hamiltonian of the molecular cluster.

All calculations has been performed using the in-house developed program MOCI (MOlecular Crystal Interactions).

3. Experimental set-up

Spectroscopic studies have been carried out in THF, toluene and decaline dilute solutions with a concentration of about 10^{-4} M. PL measurements have been performed by exciting the sample with an He–Cd laser emitting at 325 nm and collecting the signal by an Ocean Optics 2000 spectrometer with a spectral resolution of about 10 nm. Absorption measurements have been carried out with a UV–VIS spectrophotometer. PLQE were determined by comparing the emission intensity of the samples with that of a standard and normalizing the values to the absorbance. The relative accuracy of the quantum yield measurement is 10%.

Time-resolved PL measurements were made by using a Ti-sapphire mode-locked laser delivering

2 ps pulses at 82 MHz repetition rate. The luminescence was dispersed by a 0.24 m single monochromator coupled with a streak camera equipped with a two dimensional CCD. The overall time resolution was about 8 ps.

4. Results and discussion

In Table 1 we report the experimental values of PLQE and the emission peak energy in the solid-state and in dichloromethane solution [8,9], and the calculated values of the intermolecular interactions. We report the value of γ_{AB} for the molecular pairs that form the strongest H-aggregate ($H_{\max}$) and the strongest J-aggregate ($J_{\max}$), and the $t_{\mathrm{h}}^{\mathrm{sum}}$ value. The $H_{\max}(J_{\max})$-aggregates have the largest positive (negative) exciton resonance interaction. In the $H_{\max}$-aggregates molecules have typically a cofacial configuration while in the $J_{\max}$-aggregates the molecular long axis are aligned: these aggregates have the strongest influence on PLQE. For rigid compounds (DTTox, DTToxMe, ThDTToxMe) the PLQE is higher in solution than in the solid-state. The calculated $H_{\max}$ values are smaller than in the case of unsubstituted quaterthiophenes (115 meV [19]). $H_{\max}$ and $J_{\max}$ have similar values, whereas the PLQE changes up to a factor of 4. Thus, the different calculated exciton resonance interactions in the different compounds cannot explain different PLQE. We note that the computed values of γ_{AB} are exact, in the sense that they include all the multipole terms, whereas the use of the dipole–dipole approximation for these systems is not correct due to the large error it introduces, as can be seen from the values reported in parenthesis in Table 1. In particular the dipole–dipole approximation strongly overestimates the result for near molecules and can even change the sign of the interaction.

Rigid molecules in solution show very similar and high PLQE. In the solid-state, PLQE are instead much lower and with relative differences up to a factor of 4. The different PLQE of the rigid compounds can be very well related to the values of $t_{\mathrm{h}}^{\mathrm{sum}}$. Higher values means higher rate of formation of charge-transfer pairs, which decay non-radiatively, thus reducing the PLQE. In DTTox and DTToxMe X-ray analysis shows the presence of strongly interacting cofacial dimers [9], whereas the presence of the external methylated thiophene in ThDTToxMe prevents the molecules from forming close pairs.

In the case of flexible compounds (T3oxHex, DPToxHex) the PLQE in the solid-state is very high, whereas it is very low in solution. The increased PLQE in the solid-state cannot be assigned to the formation of luminescent J-aggregates. In fact the calculated values of $J_{\max}$ are very small and, furthermore, DPToxHex has higher η but smaller $J_{\max}$ than T3oxHex.

In order to investigate the causes of the PLQE increase in the solid-state, we performed TR-PL and PLQE measurements of a model system, i.e. DPTox, in solvents of different viscosity. This allows to obtain an exact quantitative determination of the non-radiative decay rates as function of the viscosity. In DPTox larger viscosity effects are expected, due to the large volume of phenyls and the absence of interactions with substituents in the β position. Results are reported in Table 2. The non-radiative decay rates strongly decrease with increasing solvent viscosity. Note that the relation between non-radiative decay rate and solvent

Table 1

PLQE in the solid-state η_{solid} and in solution ($\eta_{\mathrm{solut.}}$), emission peak energy in the solid-state ($E^{\mathrm{PL}}_{\mathrm{solid.}}$) and in solution ($E^{\mathrm{PL}}_{\mathrm{solut.}}$), exciton resonance interactions for the two molecular pairs forming the highest H-type ($H_{\max}$) and highest J-type ($J_{\max}$)-aggregate (values in parenthesis are evaluated using the dipole–dipole approximation) and averaged hole transfer integral ($t_{\mathrm{h}}^{\mathrm{sum}}$)

Sample	$\eta_{\mathrm{solid.}}$ (%)	$\eta_{\mathrm{solut.}}$ (%)	$E^{\mathrm{PL}}_{\mathrm{solid.}}$ (eV)	$E^{\mathrm{PL}}_{\mathrm{solut.}}$ (eV)	$H_{\max}$ (meV)	$J_{\max}$ (meV)	$t_{\mathrm{h}}^{\mathrm{sum}}$ (eV)
DTTox	12	75	2.4	2.7	+79 (+361)	−37 (−42)	1.807
DTToxMe	16	77	2.4	2.7	+78 (+335)	−21 (−41)	1.058
ThDTToxMe	48	85	2.2	2.3	+60 (−88)	−25 (−32)	0.343
T3oxHex	45	<1	2.3	2.3	+24 (−14)	−28 (−7)	0.112
DPToxHex	63	<1	2.5	2.5	+4 (+7)	−3 (−4)	0.001

Table 2
Measured PLQE (η) and non-radiative decay rate (k_{NR}) in solvents of different viscosity (θ), for DPTox

Solvent	θ (cP)	η (%)	k_{NR} (10^9 s^{-1})
THF	0.47	1.5	0.00911
Toluene	0.58	5.0	0.00364
Decaline	2.7	16	0.00104

viscosity is expected to be non-linear [28]. This result confirms the main role played by internal conversion in the non-radiative decay [16]. We measured a PLQE in decaline as high as 16%.

The solid-state can be considered an environment of ideally infinite viscosity, where inter-ring torsions and molecular vibrations are strongly limited by electrostatic and Van-der Waals intermolecular forces. Thus we assign the high PLQE in flexible oligothiophene-*S*,*S*-dioxides to the decrease of IC intramolecular decay rate. Furthermore the values of $H_{\max}$ and t^{sum} in T3oxHex are very small and completely negligible in DPToxHex, meaning that no other non-radiative decay channels are activated in the solid-state. Finally, we note that this environmental effect is negligible in dithienothiophene-*S*,*S*-dioxides in which the IC rate is small due to the high molecular rigidity.

The role of intermolecular interactions in the solid-state is also evident from the emission energies reported in Table 1. The emission energy difference between the solid-state and the solution is large (0.3 eV) for systems with larger intermolecular interactions (i.e. DTTox and DTToxMe), it is small (0.1 eV) for ThDTToxMe and it is negligible for T3oxHex and DPToxHex where the calculated intermolecular interactions almost vanish.

5. Conclusions

In this work we have shown that PLQE of dithienothiophene-*S*,*S*-dioxides in the solid-state can be reduced by intermolecular interactions. Theoretical calculations performed on exact crystal structures show that the trend observed in the solid-state PLQE can be assigned to different interchain interactions. On the other hand intermolecular interactions can increase the PLQE of flexible oligothiophene-*S*,*S*-dioxides, due to the increased environmental viscosity, as inferred from time-resolved PL measurements.

References

[1] H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, John Wiley & Sons, Chichester, 1997.
[2] K. Müllen, G. Wegner (Eds.), Electronic Materials: The Oligomer Approach, Wiley-VCH, New York, 1998.
[3] D. Fichou (Ed.), Handbook of Oligo and Polythiophenes, Wiley-VCH, New York, 1999.
[4] D. Oelkrug, H.J. Egelhaaf, J. Gierschner, A. Tompert, Synth. Met. 76 (1996) 249.
[5] G. Gigli, G. Barbarella, L. Favaretto, F. Cacialli, R. Cingolani, Appl. Phys. Lett. 439 (1999) 75.
[6] G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, V. Fattori, M. Cocchi, F. Cacialli, G. Gigli, R. Cingolani, Adv. Mater. 11 (1999) 1375.
[7] D. Pisignano, M. Anni, G. Gigli, R. Cingolani, M. Zavelani-Rossi, G. Lanzani, G. Barbarella, L. Favaretto, Appl. Phys. Lett. 81 (2002) 3534.
[8] G. Barbarella, L. Favaretto, G. Sotgiu, A. Bongini, C. Arbizzani, M. Mastragostino, M. Anni, G. Gigli, R. Cingolani, J. Am. Chem. Soc. 122 (2000) 11971.
[9] G. Barbarella, L. Favaretto, G. Sotgiu, L. Antolini, G. Gigli, R. Cingolani, A. Bongini, Chem. Mater. 12 (2001) 4112.
[10] Y. Kanemitsu, K. Suzuki, Y. Masumoto, Phys. Rev. B 50 (1994) 2301.
[11] M. Yan, L.J. Rothberg, F. Papadimitrakopoulos, M.E. Galvin, T.M. Miller, Phys. Rev. Lett. 72 (1994) 1104.
[12] L. Antolini, E. Tedesco, G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, D. Casarini, G. Gigli, R. Cingolani, J. Am. Chem. Soc. 122 (2000) 9006.
[13] F. Menardi, M. Cerminara, A. Sassella, A. Borghesi, P. Spearman, G. Bongiovanni, A. Mura, R. Tubino, Phys. Rev. Lett. 89 (2002) 157403.
[14] F.C. Spano, J. Chem. Phys. 118 (2003) 981.
[15] F. Della Sala, H.H. Heinze, A. Görling, Chem. Phys. Lett. 339 (2001) 343.
[16] G. Lanzani, G. Cerullo, S. De Silvestri, G. Barbarella, G. Sotgiu, J. Chem. Phys. 115 (2001) 1623.
[17] R.S. Becker, J.S. de Melo, A.L. Macanita, F. Elisei, J. Phys. Chem. 100 (1996) 18683.
[18] D. Belijonne, J. Cornil, R.H. Friend, R.A.J. Janssen, J.L. Brédas, J. Am. Chem. Soc. 118 (1996) 6453.
[19] G. Gigli, F. Della Sala, M. Lomascolo, M. Anni, G. Barbarella, A. Di Carlo, P. Lugli, R. Cingolani, Phys. Rev. Lett. 86 (2001) 167.
[20] G. Bussi, A. Ruini, E. Molinari, M.J. Caldas, P. Pusching, C. Ambrosch-Draxl, Appl. Phys. Lett. 80 (2002) 4118.
[21] A. Ferretti, A. Ruini, E. Molinari, M.J. Caldas, Phys. Rev. Lett. 90 (2003) 086401.

[22] R. Silbey, J. Jortner, S.A. Rice, J. Chem. Phys. 42 (1963) 1515.
[23] J.E. Ridley, M.C. Zerner, Theor. Chim. Acta 32 (1973) 111.
[24] D. Beljonne, J. Cornil, R. Silbey, P. Milliè, J.L. Bredas, J. Chem. Phys. 112 (2000) 4749.
[25] M.W. Wu, E.M. Conwell, Phys. Rev. B 56 (1997) R10060.
[26] M.H. Hennessy, Z.G. Soos, R.A. Pascal, A. Girlando, Chem. Phys. 245 (1999) 199.
[27] J. Cornil, D. Beljonne, J.P. Calbert, J.L. Brédas, Adv. Mater. 13 (2001) 1053.
[28] S. Sharafy, K.A. Muszkat, J. Am. Chem. Soc. 93 (1971) 4120.