The influence of crystal packing on the solid state fluorescence behavior of alkyloxy substituted phenyleneethynylenes†‡

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The study reports the solid state photophysical properties of a series of alkyloxy-substituted oligo(phenyleneethynylene)s, methoxy to hexyloxy, supported by a detailed analysis of molecular packing obtained from single crystal X-ray diffraction data. While the emission peaks are highly red shifted (by as much as 114 nm) in the solid state, all molecules exhibit similar absorption and emission in dilute solutions. The red shift is maximum in ethoxy and minimum in methoxy, while other crystalline films exhibit intermediate values. In the crystal structures, the spacing between the molecular pairs forming the J-aggregates is varied between 3.48 to 4.65 Å, with no systematic dependence on the chain length. The red shifted emission maximum is found to vary linearly with the spacing between the interacting molecules in the J-aggregate. Thus, the emission in the solid state is determined by the extent of dipolar coupling between the molecules, the alkyl chain length influencing the properties only indirectly.

Introduction

Conjugated oligomers and polymers are of immense interest in current research due to their interesting electronic and photophysical properties.[1] Recent literature contains numerous reports on the synthesis and properties of molecular systems having conjugated backbones, such as *p*-phenylenevinylenes,[2] *p*-phenyleneethynylenes,[3] *p*-phenylenes[4] and thiophenes.[5] The electronic properties exhibited by these systems have made them important in single molecular electronics[6] and display applications.[7] In addition, these molecular systems have been tested for solar cell applications[8] as well as for nonlinear optical applications such as second or third harmonic generation.[9] In contrast to their inorganic counterparts, the light emitting properties of these molecular systems are easily tunable based on structural and functional group modifications.[10]

Among the various conjugated molecules mentioned above, *p*-phenyleneethynylenes have taken centre stage as model systems with the possibility of tuning properties by way of substituting functional groups in the middle phenyl ring.[11] The last decade witnessed a lot of efforts, experimental as well as theoretical, towards designing and understanding the properties of various single molecular conductors, particularly oligo(phenyleneethynylene)s. A major portion of such studies focus on the effect of the functional groups, especially donor–acceptor pairs, on the conducting properties of the phenyleneethynylene backbone.[11a,12] Among them, the molecule carrying nitro and amino groups showed a negative differential resistance behavior, a prototype switch action.[13] In addition to the chemical effects, structural attributes such as the planarity of the phenyleneethynylene backbone also seem to have a large impact on the electronic and the photophysical properties of the *p*-phenylenethynylenes.[14] Towards this end, a number of studies have been carried out during the last decade on the molecular structure and packing in the solid state and the associated photophysical properties.[3c,15] The two-dimensional aggregation and the associated emission of merocyanine dyes in LB films have also been investigated.[16] Accordingly, the weak interactions responsible for molecular packing have come under focus in many studies.[15,17] Scanning probe microscopic techniques have also been employed to study the two-dimensional arrangements of the conjugated chains on solid surfaces.[18] A recent study on a phenyleneethynylene-phenylenevinylene copolymer has shown the photophysical properties to vary with long chain substitutions.[19] A few years ago, Bunz reviewed the literature on phenyleneethynylenes.[20]

We considered it interesting to investigate systematically the influence of crystal packing of molecules on the solid state fluorescence behavior. In this paper, we report our results on dialkyloxy-substituted oligo(phenyleneethynylene)s, where the alkyl chain length has been varied from methyl to hexyl (Scheme 1). We have obtained the crystal structures by single crystal X-ray diffraction and measured fluorescence spectra from the corresponding solid films. We have analysed the weak interactions prevalent in the crystal structures and identified the electronically interacting pairs of molecules. Our study has shown that the fluorescence emission depends directly on the molecular spacing in the crystalline state.

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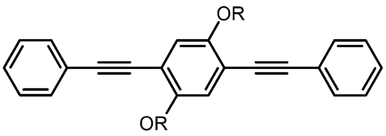
‡ Electronic supplementary information (ESI) available: Crystallographic details; NMR characterisation data; table of weak interactions; excitation spectra; XRD patterns; diagrams showing possible intermolecular interactions. CCDC reference numbers 695299–695304. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902937k



R = CH_3 (**C1**), C_2H_5 (**C2**), C_3H_7 (**C3**),
C_4H_9 (**C4**), C_5H_{11} (**C5**), C_6H_{13} (**C6**)

Scheme 1 Molecules presented in this study. R = C1: 1,4-bis(phenylethynyl)-2,5-bis(methoxy)benzene; C2: 1,4-bis(phenylethynyl)-2,5-bis(ethoxy)benzene; C3: 1,4-bis(phenylethynyl)-2,5-bis(n-propoxy)benzene; C4: 1,4-bis(phenylethynyl)-2,5-bis(n-butyloxy)benzene; C5: 1,4-bis(phenylethynyl)-2,5-bis(n-pentyloxy)benzene; C6: 1,4-bis(phenylethynyl)-2,5-bis(n-hexyloxy)benzene.

Experimental

Alkyloxy-substituted oligo(phenyleneethynylene)s (**C1**, **C2**, **C3**, **C4**, **C5** and **C6**; see Scheme 1) were synthesized following reported procedures.[21,22] All the chemicals required for synthesis were procured from a commercial source (Aldrich) and used as obtained. The solvents were distilled and dried using general procedures.[23]

Synthesis of 2,5-bis(phenylethynyl)-1,4-bis(alkyloxy)benzenes (C1–C6)

To an oven dried 100 mL two necked round bottom flask, 2,5-dibromo-1,4-dialkyloxybenzene (6 mmol) was dissolved in THF (7 ml). To the solution bis(triphenylphospine) palladium(II) dichloride (0.12 mmol) was added and stirred for 15 minutes. To the reaction mixture triphenylphosphine (0.24mmol), diisopropylethylamine (24 mmol) and copper(I)i odode (0.24) were added and the atmosphere replaced with argon (3×). To this reaction mixture phenylacetylene (14.2 mmol) was added and once again the argon atmosphere maintained and the round bottom flask was sealed. The reaction mixture was heated at 65 °C for 24 hours and filtered over celite to remove the inorganic products. The organic portion was extracted using dichloromethane and purified using flash column chromatography (silica gel and using hexanes as the eluent). The dialkyloxy-substituted oligo(phenyleneethynylene)s were produced in yields of 80 to 90% and were characterized using NMR (^{1}H and ^{13}C) spectroscopy (see ESI‡) in addition to single crystal X-ray diffraction.

Photophysical property measurements

The solution phase absorption spectra were recorded on a Shimadzu UV-3101PC UV-vis-NIR spectrophotometer while the excitation and emission spectra were recorded on a SPEX Fluorolog F112X spectrofluorimeter. Fluorescence quantum yields, with an estimated reproducibility of around 2%, were determined by comparison with diphenylanthracene ($\Phi_f = 0.9$), which was used as the standard. The fluorescence lifetimes were determined using the time-correlated single photon counting (TCSPC) technique.[24] Crystals of the compounds **C1** to **C6** were obtained by the slow evaporation of their saturated solutions in toluene and the crystals were separated from the mother liquor. For solid state photoluminescence measurements, the crystals were spread in between two glass plates and heated to melting and slowly cooled to room temperature. Fluorescence measurements of the films were carried out using the front face emission scan mode on the SPEX Fluorolog F112X spectrofluorimeter. Solid state quantum efficiency was measured using a calibrated integrating sphere in the SPEX Fluorolog spectrofluorimeter. A Xe arc lamp was used to excite the thin film sample placed in the sphere, with 360 nm excitation wavelength. The solid state quantum yield was determined by comparing the spectral intensities of the lamp and sample emission using a reported procedure.[25] In order to test the calibration of the experimental system, the solid state quantum yield of a thin film of Alq_3 was determined (0.19), which is consistent with previously reported values.[25]

Crystallography measurements

In order to carry out X-ray diffraction measurements, the recrystallised samples were analyzed under a polarizing microscope and single crystals were separated for X-ray structure determination. The single crystal data were collected on a Bruker-Nonius diffractometer with Kappa geometry attached with an APEX - II-CCD area detector and a graphite monochromator for Mo Kα radiation (50 kV, 40 mA) at room temperature (298 K). The intensity data were processed using SAINT software[26] of the Bruker suite of programs. The structures were solved and refined using the SHELXTL package.[27] The structure was solved by direct methods and refined by full-matrix least-squares techniques. All hydrogen atoms were located from a difference Fourier map. The intermolecular interactions were analyzed using the PLATON package.[28] The crystalline nature of the film samples used for solid state fluorescence was confirmed by performing diffraction on a Bruker D8 system. The obtained patterns matched well with the powder patterns simulated based on the single crystal data (see ESI‡ Fig. S3).

Results and discussion

The solution phase absorption spectra of **C1** to **C6** recorded from their dilute toluene solutions (15 μM) are shown in Fig. 1a. The absorption spectra exhibit two intensity maxima centered around 307 and 367 nm. The presence of two features in the absorption spectrum is understandable. A theoretical study[29] on **C6** has shown that in solution, the molecule exists in the planar form and the alkyloxy-substitution modifies the π-orbitals of the central arene ring through resonance interaction with the oxygen lone pairs resulting in electronic transitions from both HOMO and HOMO − 1 to LUMO. The scenario is expected to be similar in other molecules as well. Fig. 1b shows the fluorescence emission spectra of the compounds **C1** to **C6**. All the molecules exhibit similar spectral features with the maximum intensity around 401 nm and a shoulder at ~420 nm. As the emission behavior is essentially similar, the chain length (alkyloxy) induced chemical effects should have a minimal role, if any. The excitation spectra (see ESI,‡ Fig. S1) showed features with maxima at 310 and 367 nm, similar to the absorption spectra (Fig. 1a), indicating that the absorbing and the emitting species are similar in all the molecules. Table 1 lists the details of the absorption and emission characteristics of the molecules in solution. In all the cases, the emission exhibited a monoexponential decay confirming the

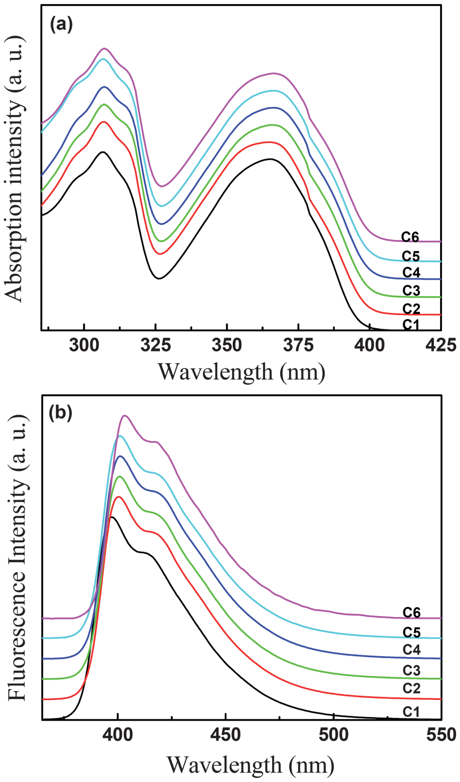


Fig. 1 (a) Absorption in dilute solutions (15μM in toluene) and (b) fluorescence in dilute solutions (excitation wavelength, 360 nm) of alkyloxy-substituted oligo(phenyleneethynylene)s.

Table 1 Absorption and emission properties of alkyloxy substituted oligo(phenyleneethynylene)s (15μM) in toluene

Molecule	$\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}	τ (ns)	χ^2	Φ(Fl.)
C1	3.198	1.23	1.02	0.90
C2	2.964	1.32	1.01	0.92
C3	3.001	1.37	1.07	0.91
C4	3.209	1.45	1.05	0.91
C5	3.186	1.45	1.02	0.89
C6	3.093	1.35	1.09	0.91

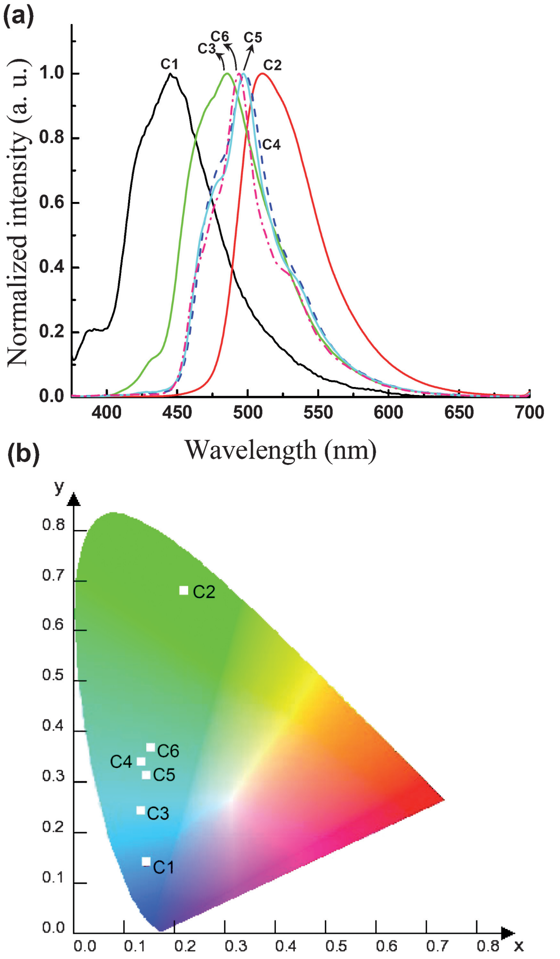


Fig. 2 (a) Fluorescence emission (excitation 360 nm) spectra for the crystalline films of **C1** to **C6**. (b) Chromaticity diagram (CIE 1931) showing the emission colours.

presence of a single emitting species. Singlet excited state lifetimes of **C1** to **C6** lie within a narrow range of 1.23 to 1.45 ns with no systematic dependence on the chain length. All the molecules showed a high quantum yield of ~0.9.

The solid state behavior of the molecules is quite different. Fig. 2 shows the fluorescence spectra from the crystalline films of **C1** to **C6**. On comparing the behavior in solution (see Fig. 1b), we find that the solid state emission peaks are red shifted. The spectrum from **C1** exhibits the maximum emission intensity at ~444 nm with distinct shoulders at 425 and 390 nm and a broad tail at higher wavelengths. With an increase in the chain length by one methylene unit, the **C2** spectrum is highly red shifted to around 515 nm, and it is relatively symmetric. The spectra of **C3**, **C4**, **C5**, and **C6** lie between those of **C1** and **C2**, with **C4**, **C5** and **C6** almost overlapping. Thus, a systematic trend in the variation of the emission with alkyloxy chain length is not quite apparent from this data. In the excitation spectra shown in Fig. S2 (ESI‡), a number of intensity maxima are observed indicating the presence of various emitting levels in the crystalline state. The emission colors from the crystalline samples are represented with the help of a chromaticity diagram, CIE 1931 standard (see Fig. 2b). The **C1** system lies in the blue region while **C2** is distinctly in the green region and the rest of the molecules exhibit intermediate colors in the crystalline state.

In order to gain an insight into the solid state fluorescence behavior of the various molecules, it is important to look into the details of the molecular packing in their single crystals. Single crystals can be considered as self-assembled species par excellence since the nature of the weak interactions between neighboring molecules can be determined with a high degree of precision.[15] These intermolecular forces typically decide the bulk alignment of the molecules and thereby the photophysical properties of the materials. In the present study, we have carried out fluorescence measurements on crystalline films. The XRD patterns from the films were essentially similar compared to the simulated powder patterns from the single crystal data (Fig. S3, see ESI‡).

All the dialkyloxy-substituted oligo(phenyleneethynylene)s (**C1** to **C6**) crystallize in monoclinic space groups (*C*2/*c*, *P*2$_1$/*c* or *P*2$_1$/*n*) with a half molecule in the asymmetric unit. The crystal

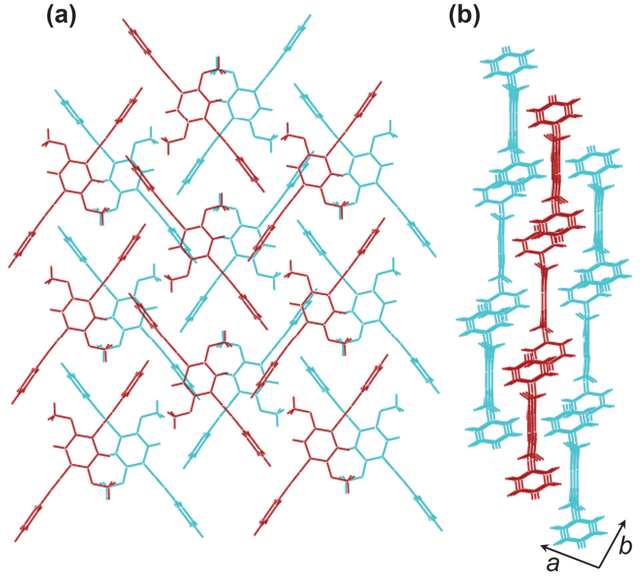


Fig. 3 (a) Herringbone packed layers of **C1** along the *ac*-diagonal plane of the crystal lattice. (b) A lateral view of the slipped stack of molecular layers.

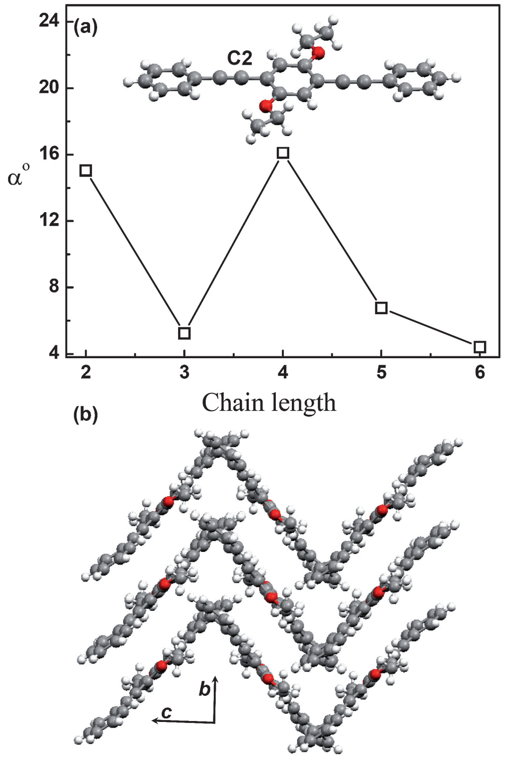


Fig. 4 (a) Deviation of the phenyl ring from planarity with respect to the alkyl chain length. (b) Herringbone packing of molecule **C2**.

structures of compound **C6** is previously known in the literature and the structure solution obtained in this study matched closely with that reported.[17b] The crystal structures of **C1**, **C2**, **C3**, **C4** and **C5** are being reported by us for the first time. Crystallographic and refinement details of the compounds are provided in the ESI‡ (Table S1). Obviously, the molecular geometry varies depending on the alkyl chain length. The molecule **C1** shows a maximum deviation from planarity in contrast to the usual planar geometry of phenyleneethynylenes.[30] The end phenyl rings are twisted by as much as $\sim$80° in relation to the middle ring. The crystal structure shows a slipped herring bone packing along the *ac*-diagonal plane as shown in Fig. 3a. Fig. 3b contains three molecular layers in the lateral view. The major interactions in crystal packing are C–H$\cdots\pi$ in nature, where the triple bond serves as a π acceptor for four interactions originating from the phenyl ring hydrogens. The stability provided by the C–H$\cdots\pi$ interactions is primarily responsible for such an unfavorable twist in the molecule. The deviations of the middle phenyl ring from the planarity in the other molecules, **C2** to **C6**, are within the range of 4.5° to 16° as shown in Fig. 4a. These molecules adopt a herringbone type of packing arrangement as shown in Fig. 4b taking **C2** as example. The alkyl chain in **C3** exhibits a *gauche* conformation, while in the other molecules, the chains are in *trans* conformation. The C–H$\cdots\pi$ interactions in these structures originate from both phenyl and alkyl chain hydrogens with both the phenyl ring and the triple bond acting as π-acceptors. In **C4**, we found an additional interaction of C–H$\cdots$O type. The details of hydrogen bonding are listed in Table S2 (ESI‡). The interchain interaction seems to build up as the chain length increases and accordingly the distance between them, as measured with respect to lines drawn bisecting the methylene chains, varies as 4.85, 4.31 and 3.88 Å for **C4**, **C5** and **C6** respectively.

A detailed analysis of the molecular packing revealed that for each molecule, there exist two neighbors. Thus, one finds two types of molecular pairs as shown for **C1** in Fig. 5. In Fig. 5a, the partner molecules extend an angle of 78.5° between them, while in Fig. 5b the pair is parallel with a spacing of 4.65Å. Based on earlier theoretical and experimental studies, it is reasonable to consider the first pair (Fig. 5a) to be weakly interacting or non-interacting.[31] In the second pair (Fig. 5b), the molecules are arranged in a nearly 'head to tail' fashion, akin to a 'J-aggregate'.[32] However the intermolecular distance is fairly large (4.65Å) which would result in minimal electronic communication between the two molecules. The molecular packing pattern of the interacting molecules was similar in all the cases (Fig. S4 to S8, see ESI‡). Depending on the C–H$\cdots\pi$ interactions prevalent, the spacing between the interacting molecules is found to vary in the range 3.48–4.62 Å. This class of molecules prefer to remain in all-planar conformation while the solid state packing can bring about significant distortions affecting the intermolecular spacing

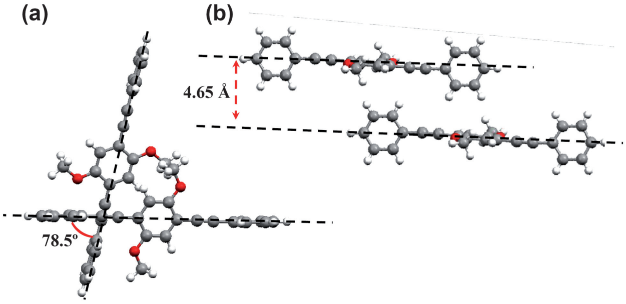


Fig. 5 (a) Crossed and (b) slipped stacking pairs in molecule **C1**.

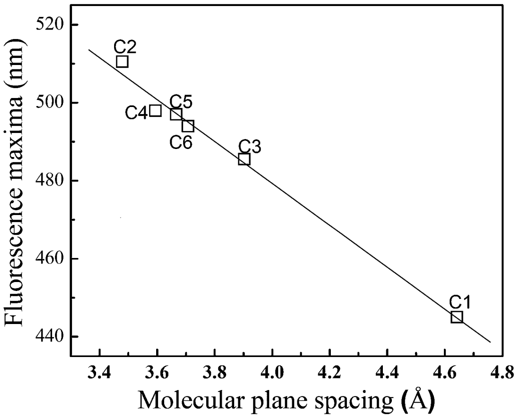


Fig. 6 Variation of the emission maximum with the spacing between the interacting molecules in crystals of **C1** to **C6** (excitation 360 nm).

and in turn the transition energies.[30] An interesting correlation was observed between the solid state emission maxima (from Fig. 2a) and the spacing between the interacting molecules forming the J-aggregates. As presented in Fig. 6, the emission maximum shows a linear dependence on the molecular spacing, exhibiting a blue shift with increasing spacing. This is not only a clear indication of the presence of J-aggregates, but is also clearly a measure of the strength of the dipolar coupling between the interacting molecules.[33,34] Such a direct correlation between the crystal packing and the emission property is indeed noteworthy. Corresponding to emission from the dilute solutions (401 nm), a spacing value of 5.55 Å can be derived from the plot in Fig. 6. This value should indicate a very weakly coupled aggregate structure.

We have also performed an experiment to physically influence the aggregate structure by way of breaking up the crystals into smaller and smaller particles. This was accomplished by gently grinding known quantities (14.4 μg, 7.2 μg and 3.6 μg) of **C6** crystals with 100 mg of dry KBr powder. The spectra obtained (Fig. 7) are blue shifted with respect to pristine **C6**. The intensity maximum in the sample containing 14.4 μg of **C6** occurs at 462 nm which remains nearly the same in the case of the 7.2 μg sample albeit with reduced intensity. Both spectra do contain a shoulder feature around 494 nm corresponding to the parent aggregate structures. The blue shifted emission is likely to arise due to the microcrystalline nature of the sample where the J-aggregates near the particle surface may suffer from a reduced interaction in contrast to those in the bulk lattice. We observe a rise in intensity around 400 nm due to increasing proportions of the isolated molecular species from the surface. On further diluting the sample (3.6 μg in KBr), the emission from both surface (462 nm) and bulk species (494 nm) diminishes while emission due to monomeric species (400 nm) increases further. This is understandable as the concentration of the emitting species is in the nanomolar range.[15b,35] The fluorescence spectrum of the isolated monomeric species matches closely with the solution phase spectrum of **C6**.

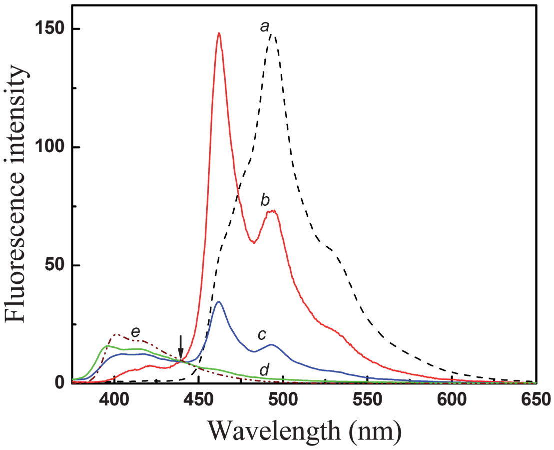


Fig. 7 Fluorescence spectra (excitation 360 nm) of **C6**. Fluorescence from the crystalline film, spectrum *a* (as in Fig. 2a). The spectra *b*, *c* and *d* correspond respectively to 14.4, 7.2 and 3.6 μg of **C6** diluted with 100 mg of KBr powder. The isosbestic point observed at 440 nm is marked with an arrow. The solution phase spectrum (*e*) is shown for comparison with arbitrary intensity.

Table 2 Fluorescence lifetimes and quantum yields of dialkyloxy-substituted oligo(phenyleneethynylene)s in the solid state

	Lifetime (ns)							
Compound	τ_1	$F_1\%$	τ_2	$F_2\%$	τ_1	$F_3\%$	χ^2	Φ (solid)
C1	2.83	61	4.59	25	0.72	14	1.01	0.51
C2	3.10	55	4.68	42	0.35	3	1.01	0.53
C3	2.24	84	0.24	4	4.13	12	1.06	0.82
C4	0.22	3	2.63	97	—	—	1.07	0.73
C5	2.22	66	0.27	3	3.35	31	1.01	0.74
C6	0.20	2	2.55	95	5.29	3	1.01	0.78

Table 2 shows the summary of the fluorescence lifetime measurements. All the compounds show tri-exponential decay except the molecule **C4**, which shows a bi-exponential decay with the longest lifetime species as the major one. Molecule **C2** shows two lifetimes with comparable relative abundance, whereas for molecules **C1**, **C3**, **C5** and **C6** the species with intermediate lifetime are the major components. All the crystals exhibited quantum yields (up to 0.8) but these are low compared to the values from the solution phase (compare Tables 1 and 2). Also, there is a spread in the values (0.51–0.82) in the crystalline state which is absent in solution. A systematic trend with respect to the alkyl chain length is however not quite obvious. When examined with respect to the weighted average of lifetime, a trend seems to emerge: the higher the lifetime, the less the quantum yield, implying that the decay of the excited state take place through non-radiative channels.

Conclusions

The present study deals with the crystal structures and the fluorescence properties of alkyloxy-substituted oligo(phenyleneethynylene)s (methyl, **C1**, to hexyl, **C6**). The crystalline films of **C1** and **C2** exhibit fluorescence maxima at ~444 and 515 nm respectively, while for **C3**, **C4** and **C5**, the maxima are positioned in between, with hardly any trend with respect to the chain length. This is in clear contrast to the behavior in dilute solutions, where all the molecules, **C1** to **C6**, exhibit fluorescence maxima around 401 nm. An analysis of the crystal packing of the molecules revealed the presence of J-aggregate pairs, which accounted for the red shifted emission in the solid state. Interestingly, the emission maximum was found to vary linearly with the spacing between the interacting pair of molecules in the J-aggregates: the lower the spacing, the greater the red shift. In dilute solutions, the molecules exhibited monoexponential decay of the excited state with high quantum yields (~0.9). In the case of the crystalline films, the quantum yields were still appreciable but varied (0.5 to 0.8).

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