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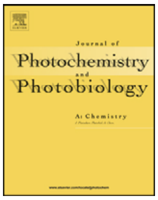

Short communication

Photophysics and self-assembly of symmetrical and unsymmetrical cationic oligophenylene ethynylenes

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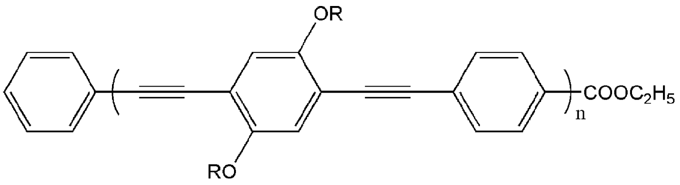
ABSTRACT

A study of the synthesis, photophysical behavior and self-assembly of a series of symmetrical cationic oligophenylene ethynylenes is reported. Aqueous solutions of all these compounds exhibit strong and structured absorption in the ultraviolet (maxima near 305 nm and 355 nm) with a broad fluorescence in the range 370–600 nm. While all of these compounds show strong fluorescence in methanol, the fluorescence yields in water are variable and substituent dependent. Transient absorption, presumably attributable to a triplet is found for all of the oligomers studied thus far. All of the compounds having a net positive charge exhibit strong complex formation when they are added to aqueous solutions containing the anionic biopolymer carboxymethylcellulose. The complexes are characterized by a pronounced red shift in the oligomer absorption spectrum and a red shifted and generally intense fluorescence. We attribute the spectral shifts due to the formation of "J-dimers" in each case. The results of this preliminary study suggest that these compounds may be useful in sensing due to their strong tendency to associate with anionic biomacromolecules.

There has been much recent interest in oligomeric conjugated polymers and especially oligomeric phenylene ethynylenes [1–9]. The latter are interesting due to their rigid rod-like structures that impart useful properties for a number of applications [10–12]. We have recently initiated a study of the synthesis, photophysics, self-assembly and antimicrobial activity of a series of cationic oligomeric phenylene ethynylenes (OPEs) having the structure **1**, where *n* ranges from 1 to 4 [13]. Structure **1** was chosen so that these OPEs could be studied in aqueous solution, in colloidal suspensions and attached (by the modification of the carboxyester "headgroup") onto surfaces by various covalent linkages. In our initial examination of these compounds where $n = 1$ and 2 we were interested in the finding that while the two compounds show similar absorption and fluorescence spectra in water and methanol, the fluorescence in water is much weaker [13]. The synthesis of the unsymmetrical derivatives of the series **1** is much more difficult than the synthesis of symmetrical molecules having structures such as **2** since the symmetrical molecules can be built by adding the same unit to both sides of a symmetrical diiodobenzene derivative. In line with our finding that OPE-1 (where $n = 1$) exists as a monomer in both methanol and water and weakly fluorescent solutions of OPE-1 in water become highly fluorescent when exposed to the anionic biopolymer carboxymethylcellulose (CMC) possibly through the formation of a "J-dimer", [14,15] we decided to investigate the series of derivatives of **2** where X = H (S-OPE-1), $X = CO_2Et$ (S-OPE-1 (COOEt)) and $X = COO^-$ (S-OPE-1 (COO^-)) and to compare the photophysical behavior and self-assembly processes that occur for this series of symmetrical compounds with those of the unsymmetrical OPE-1. Synthesis and purification of these compounds are included as supplementary material. The characterization of the compounds was by proton and carbon NMR.



1 where $R = CH_2CH_2CH_2N(CH_3)_3^+$

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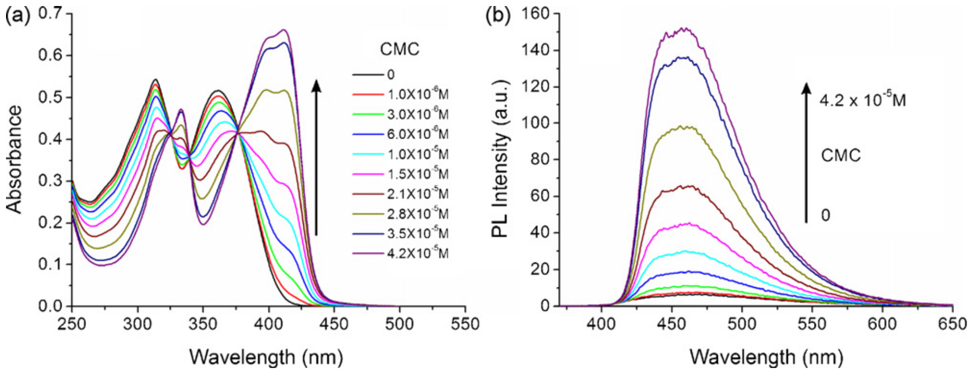
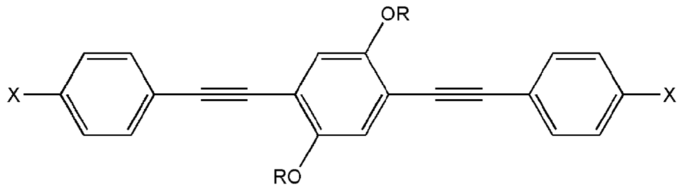


Fig. 1. Absorption spectral changes (a) and fluorescent spectral changes (b) upon addition of aliquots of CMC to an aqueous solution of S-OPE-1 (COOEt). [S-OPE-1 (COOEt)] = 15 μM, [CMC] = 0–42 μM, λ_{ex} = 362 nm.



2 X = H, CO_2Et, COO^- where R = $CH_2CH_2CH_2N(CH_3)_3^+$

All three of the symmetrical molecules, S-OPE-1 (H), S-OPE-1 (COOEt) and S-OPE-1 (COO$^-$) show similar two-banded absorption spectra in water and methanol. The absorption spectrum of S-OPE-1 (COOEt) is shown in Fig. 1; the absorption and fluorescence maxima for all four compounds are listed in Table 1. The spectra are concentration independent in the micromolar concentration range and there is a small red shift in the series: S-OPE-1 (H), OPE-1~S-OPE-1(COO$^-$), and S-OPE-1 (COOEt). Each of the compounds also exhibits a relatively broad structureless single fluorescence transition with maxima in the range 397–472 nm for both methanol and aqueous solutions [16]. The fluorescence of all four compounds is strong in methanol (Table 1) and there is little variation in fluorescence efficiency among the different substituted derivatives. However there is a significant variation in the fluorescence efficiencies in aqueous solution ranging from 0.02 for S-OPE-1 (COOEt) to 0.80 for S-OPE-1 (H). While the diester derivative S-OPE-1 (COOEt) shows a very low fluorescence quantum efficiency [17] in water, the dicarboxylate derivative shows very strong fluorescence in aqueous solution near neutral pH. Clearly the ester groups in OPE-1 and S-OPE-1 (COOEt) must play a major role in a solvent-dependent process, which deactivates the excited singlet of the oligomers in water [16]. Nanosecond transient absorption spectroscopy was carried out on the OPEs in order to monitor the triplet states. For all four compounds in aqueous solution transients giving rise to broad transient absorption bands were observed in the mid-visible region with lifetimes in the microsecond range (Table 1). The transient lifetimes and spectra are consistent with a triplet state assignment [18]. The λ_{max} of triplet–triplet absorption shifts from 518 nm to 569 nm following the extent of conjugation: S-OPE1-H (518 nm), OPE1 (533 nm), S-OPE-1 (COO$^-$) (557 nm), then S-OPE-1 (COOEt) (569 nm). The apparent triplet yields decrease in the order of S-OPE-1 (H) > S-OPE-1 (COO$^-$) ≫ OPE-1 ≈ S-OPE-1 (COOEt). The triplet lifetimes follow a similar trend as the triplet yield (Table 1). Interestingly, the relatively low triplet yield for S-OPE-1 (COOEt) mirrors the low fluorescence quantum yield, suggesting that the triplet formation is suppressed by the same mechanism that quenches the singlet state.

The three cationic oligomers, S-OPE-1 (H), OPE-1 and S-OPE-1 (COOEt) all show striking changes in absorption and fluorescence when CMC (Sigma–Aldrich, degree of carboxyl substitution (DS) = 0.7) is added to aqueous solutions (oligomer concentration ~15 μM) in the μM concentration range. Fig. 1 shows a series of spectra for addition of CMC to S-OPE-1 (COOEt). Similar spectral changes, but with less pronounced red shifts, are observed over the same concentration range for S-OPE-1 (H) and OPE-1 [16]. Interestingly, there are no changes observed when a similar study is made for S-OPE-1 (COO$^-$) with CMC at near neutral pH. The changes that occur for S-OPE-1 (H), OPE-1 and S-OPE-1 (COOEt) (sharp, red shifted absorption spectra, isosbestic points maintained throughout the CMC addition and red shifted fluorescence) are consistent with an extension of effective conjugation for the oligomers on the carboxylate decorated surface of the CMC. The fluorescence quantum efficiency of the oligomer:CMC complex shows a dramatic increase for S-OPE-1 (COOEt) (more than 18-fold), a strong increase for OPE-1 and very little change for S-OPE-1 (H) (see Table 1). The spectroscopic behavior of S-OPE-1 (COOEt) with CMC is reminiscent of the formation of cyanine J-aggregates templated on carboxymethylamylose and CMC [19–21]. The increase in effective conjugation could be attributed either to planarization [22] or to formation of J-dimers [19,20]. Structurally similar OPE's have been investigated in organic solvent systems; although there is indicated to be little barrier to rotation of the phenyl rings from a totally coplanar structure, the completely planar system is estimated to

Table 1
Fluorescence quantum efficiencies[a] and lifetimes of OPE-1, S-OPE-1 (H), S-OPE-1 (COO$^-$), and S-OPE-1 (COOEt).

	Abs. (nm)	Em. (nm)	ϕ_f in H_2O	τ (ns)	τ_{TA} (μs)	ϕ_f in CH_3OH	τ (ns)
OPE-1	303, 355	420	0.15 ± 0.018	1.5	107	0.68 ± 0.028	1.6
S-OPE-1 (H)	303, 348	397	0.80 ± 0.011	1.6	216	0.82 ± 0.030	1.4
S-OPE-1 (COO$^-$)	310, 355	422	0.70 ± 0.010	1.5	136	0.74 ± 0.042	1.3
S-OPE-1 (COOEt)	314, 362	465	0.023 ± 0.001	1.0	77	0.75 ± 0.019	1.4
OPE-1/CMC[b]	325, 381	472	0.34 ± 0.004				
S-OPE-1 (H)/CMC[c]	308, 318, 367	423	0.81 ± 0.017				
S-OPE-1 (COOEt)/CMC	333, 412	458	0.39 ± 0.023				

[a] The standard is quinine sulfate.

[b],[c] The quantum efficiency is obtained where the concentration of OPE-1 or S-OPE-1 (H) is 1 × 10^{-5} M.

be a slight energy minimum [23]. Additionally in this experimental and computational study the absorption spectrum calculated for a completely planar structure is similar to those shown in Fig. 1 and Table 1 and also to that found for the OPE studied experimentally [23]. As with other cases of host–guest complex formation in aqueous media, the formation of a planarized monomer or J-dimer of the oligomers on CMC is likely attributable to a combination of favorable Coulombic and hydrophobic interactions between the host and guest with favorable molecular topographies either pre-existing or induced during the complex formation. The failure of S-OPE-1 (COO^-) to interact with CMC is not surprising since it should be a zwitterion at neutral pH and thus there should be no Coulombic attraction towards the CMC host.

The sharply reduced fluorescence of the two ester containing oligomers, OPE-1 and S-OPE-1 (COOEt) in aqueous solution, compared to methanol, is remarkable and unprecedented for simple aromatic esters. While we do not yet know the origin of these effects, we have found that other S-OPE-1 with different substituents ($X = NH_2$, $COCH_3$) exhibit similar reduced fluorescence in water [24].

The strong spectral red shifts in both absorption and fluorescence coupled with the increase in fluorescence efficiency upon complexation with CMC, suggest that S-OPE-1 (COOEt) and other oligomers having extended π conjugation may be useful in sensing applications similar to those already demonstrated for certain cationic cyanines and anionic biopolymers such as hyaluronic acid and DNA [20]. It is striking that excitation of S-OPE-1 (COOEt) in water at 412 nm results in an increase from essentially no fluorescence at 458 nm to a very strong fluorescence easily detectable at micromolar concentrations of CMC repeat units. Since oligomers having extended symmetrical structures from the structure of **2** can be readily generated with a variety of substituents and other structural features, it should be possible to generate a versatile library of dyes and fluorescent probes extending into the visible region.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.03.006.

References

[1] J.M. Tour, Chem. Rev. 96 (1996) 537–553.
[2] J.S. Moore, Acc. Chem. Res. 30 (1997) 402–413.
[3] L. Jones, J.S. Schumm, J.M. Tour, J. Org. Chem. 62 (1997) 1388–1410.
[4] U. Ziener, A. Godt, J. Org. Chem. 62 (1997) 6137–6143.
[5] H. Kukula, S. Veit, A. Godt, Eur. J. Org. Chem. 1999 (1999) 277–286.
[6] J.N. Wilson, U.H.F. Bunz, J. Am. Chem. Soc. 127 (2005) 4124–4125.
[7] M.I. Sluch, A. Godt, U.H.F. Bunz, M.A. Berg, J. Am. Chem. Soc. 123 (2001) 6447–6448.
[8] P.K. Sudeep, P.V. James, K.G. Thomas, P.V. Kamat, J. Phys. Chem. A 110 (2006) 5642–5649.
[9] K.-Y. Pu, X.-Y. Qi, Y.-L. Yang, X.-M. Lu, T.-C. Li, Q.-L. Fan, C. Wang, B. Liu, H.S.O. Chan, W. Huang, Chem. Eur. J. 14 (2008) 1205–1215.
[10] I.-B. Kim, A. Dunkhorst, J. Gilbert, U.H.F. Bunz, Macromolecules 38 (2005) 4560–4562.
[11] M.D. Disney, J. Zheng, T.M. Swager, P.H. Seeberger, J. Am. Chem. Soc. 126 (2004) 13343–13346.
[12] K. Liu, G. Li, X. Wang, F. Wang, J. Phys. Chem. C 112 (2008) 4342–4349.
[13] Y.L. Tang, Z.J. Zhou, K. Ogawa, G.P. Lopez, K.S. Schanze, D.G. Whitten, Langmuir 25 (2009) 21–25.
[14] N. Maiti, C. Nakul, M. Ravikanth, S. Mazumdar, N. Periasamy, J. Phys. Chem. 99 (1995) 17192–17197.
[15] F. Del Monte, M.L. Ferrer, D. Levy, Langmuir 17 (2001) 4812–4817.
[16] We have synthesized and carried out preliminary studies of S-OPE-1 (X) where $X = NH_2$, $COCH_3$. Both of the compounds show similar absorption spectra to that shown in Fig. 1.
[17] J.R. Lakowicz, Principles of Fluorescence of Spectroscopy, Kluwer Academic/Plenum Publisher, New York, 1999.
[18] K.A. Walters, K.D. Ley, K.S. Schanze, Chem. Commun. (1998) 1115–1116.
[19] O.-K. Kim, J. Je, G. Jernigan, L. Buckley, D.G. Whitten, J. Am. Chem. Soc. 128 (2006) 510–516.
[20] D.G. Whitten, K.E. Achyuthan, G.P. Lopez, O.-K. Kim, Pure Appl. Chem. 78 (2006) 2313–2323.
[21] Z.J. Zhou, Y.L. Tang, D.G. Whitten, K.E. Achyuthan, ACS Appl. Mater. Interfaces 1 (2009) 162–170.
[22] T. Miteva, L. Palmer, L. Kloppenburg, D. Neher, U.H.F. Bunz, Macromolecules 33 (2000) 652–654.
[23] P.V. James, P.K. Sudeep, C.H. Suresh, K.G. Thomas, J. Phys. Chem. A 110 (2006) 4329–4337.
[24] It is worth noting that the S-OPE-1 (COOEt) exhibits a much greater reduction in efficiency than OPE-1 and thus the substituent effect for the symmetrical molecules is much more than additive in this case.