Pergamon

Tetrahedron Letters 40 (1999) 3239–3242

TETRAHEDRON
LETTERS

Molecular triads of soluble oligo-2,6-naphthylenevinylenes end-capped with [60]fullerene

José L. Segura and Nazario Martín*

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain.

Received 7 January 1999; accepted 17 February 1999

***Abstract*:** Novel soluble oligo-2,6-naphthylenevinylenes linked to two [60]fullerene units have been prepared from the corresponding highly fluorescent diformyl-oligo-2,6-naphthylenevinylene through 1,3-dipolar cycloadditions to C_{60}. The fluorescence spectrum of the triad formed shows a strong quenching of the fluorescence of the oligonaphthylenevinylene moiety thus suggesting a fast photoinduced electron transfer from the excited oligomer to the C_{60} moiety. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords : Oligomers ; Fullerenes ; Electron transfer ; Cycloadditions

Photoinduced electron transfer from conducting polymers derived from polyphenylene vinylene (PPV) or oligothiophene and C_{60} have been reported by Sariciftci et al. in a series of papers.[1-5] The fluorescence in the conducting polymer is quenched by the presence of C_{60} molecules. These polymer-C_{60} systems have been used to prepare improved polymeric photovoltaic cells with high efficiency,[2] being one of the most outstanding applications of buckminsterfullerenes. While the forward electron transfer reaction occurs in a subpicosecond time scale, the recombination of the photogenerated electrons on fullerenes and the holes in the polymer is slow (> μs). Among other donor-linked fullerenes,[6,7] the study of photoinduced electron transfer in molecular dyads and triads of conjugated oligomers covalently linked to fullerenes has been proposed in order to investigate whether this large difference in electron transfer rates is an intrinsic property of the structures involved.[8] Oligomers are well-structured molecules which allow the establishment of a relationship between structural effects and electronic properties of the related polymers and are interesting materials for applications in opto-electronics.[9-11]

---

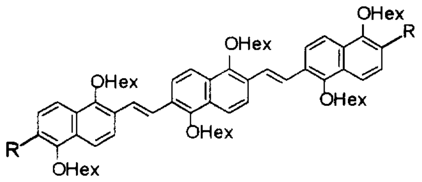
* e-mail : nazmar@eucmax.sim.ucm.es

PII: S0040-4039(99)00373-1

In this context, although a few dyads in which the oligomer is covalently attached to a C_{60} unit have been recently reported,[8,12] only one example has been reported in which the oligomer is end-capped with two C_{60} units.[8] In this communication we report the preparation of covalently linked [60]fullerene-oligo-2,6-naphthylene vinylene (ONV) derivatives, their UV-Vis absorption and emission properties as well as their electrochemical characterization.

Amongst the suitable procedures for the functionalization of [60]fullerene, the 1,3-dipolar cycloadditions of azomethine ylides to C_{60} play a prominent role.[13,14] We have selected this synthetic approach for the preparation of the target dyads **3** which were obtained by reacting sarcosine, [60]fullerene and the formylsubstituted trimeric material **1** in refluxing toluene for 48 h.

Despite the facility with which C_{60} enters into these intermolecular dipolar cycloaddition reactions, little attention has been accorded to the preparation of triads probably as a consequence of the lack of solubility of the final adducts containing two fullerene units.[15-18] Therefore, as the oligomeric material we chose the electron-rich, highly fluorescent, functionalized naphthylenevinylene trimer **2** whose electrochemical and PL properties have been recently studied in our group[19] and in which the presence of polyhexyloxy substitution allowed us to obtain highly soluble adducts which could be purified by flash chromatography (neutral silica gel, cyclohexane and toluene : cyclohexane, 8:2).



1: R = CHO
2: R = H

Figure 1

In agreement with the chiral character of the unsymmetrical carbon of the pyrrolidine units, two different bands could be observed in the thin layer chromatograms (cyclohexane : Toluene 1 : 1) of **3** (20% yield) which are reasonably assigned to the *meso* and the *racemic* isomers which could be also separated by careful flash chromatography.

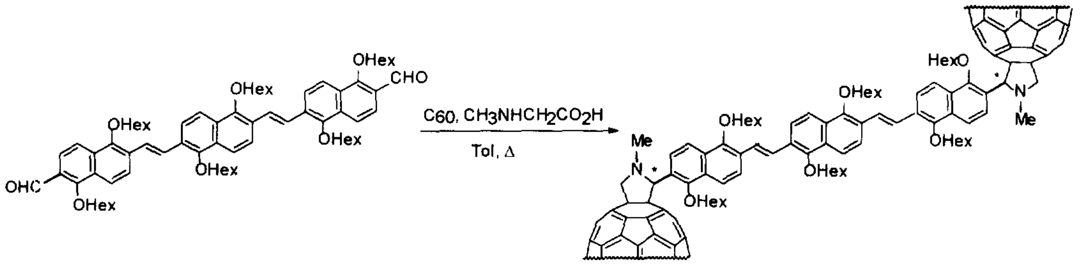
The good solubility imparted by the alkoxy chains allowed full spectroscopic and electrochemical characterization of triads **3**[1] and the results obtained have been compared with those observed for the unsubstituted trimer **2**. The redox properties of the first eluted and major diastereomer were studied by cyclic

---

[1] Selected spectroscopic data for triad **3** (first eluted, major diastereomer) : FT-IR (KBr, cm^{-1}) : 2921, 2852, 1628, 1459, 1405, 1335, 1024526 ; UV-Vis (CH_2Cl_2) : 256, 310 (sh), 330 (sh), 398, 420 nm ; ^{1}H-NMR ($CDCl_3$, 300 MHz) : 8.18 (d, 2H, J = 8.9 Hz), 8.00 (d, 2H, J = 8.9 Hz), 7.88 (dd, 4H, J = 13.4 Hz), 7.87 (br s , 4H), 7.73 (br s, 4H), 5.60 (s, 2H), 5.04 (d, 2H, J = 9.4 Hz), 4.34 (d, 2H, J = 9.4 Hz), 4.19 (t, 4H), 4.05 (m, 8H), 2.81 (s, 6H), 2.02 (m, 12H), 1.68 (m, 12H), 1.43 (m, 24H), 0.95 (m, 18H).

voltammetry in toluene: acetonitrile (5 : 1) at room temperature. The voltammogram shows four quasireversible reduction waves at $E_{1/2}$= -0.65 ; -1.05 ; - 1.62 and –1.93 V corresponding to the fullerene moiety, in addition to another reduction wave at $E_{1/2}$ = -1.22 V which is assigned to the reduction of the oligomer unit. An oxidation wave is poorly observed at around 1.4 V due to the oxidation of the oligomer. This assignment was confirmed by comparison with the CV of the parent oligomer (**2**).

It is interesting to note that the reduction potentials are shifted to more negative values than the parent C_{60} as observed for most 1,2-dihydrofullerenes.[20,21] In this case, the CV data have an analytical and structural character since the presence of both chromophores are clearly observed, thus confirming the proposed structure.



1

3r: racemic-form
3m: meso-form

Scheme 1

The absorption spectrum of **3** in dichloromethane (Figure 2) is essentially a simple superimposition of the absorption spectra of the C_{60} and the trimeric moiety. Therefore, we conclude that there is no significant inter or intramolecular charge transfer between the C_{60} and the trimeric unit in the ground state which is in agreement with that observed for composites of C_{60} and fluorescent conjugated organic polymers.[5] Figure 2 shows also the fluorescence spectrum in dichloromethane of unsubstituted trimer **2** upon excitation at 398 nm exhibiting emission maxima at 427, 455 and 485 nm. When triads **3** were irradiated at this wavelength no fluorescence was observed. This result strongly indicates that the photoinduced charge separation is a faster process than the back transfer and therefore the fluorescence of the trimeric moiety is efficiently quenched.

In summary, we have established that oligoarylenevinylenes can be conveniently attached to the C_{60} framework to form highly soluble C_{60}-based triads in which the fluorescence of the oligoarylene moiety is strongly quenched. Work is in progress to prepare other functionalized fluorescent oligoarylenes emitting in different spectral regions ranging from the UV to the near-IR. Study of the photophysical properties of the conjugated oligomer-fullerene arrays and comparison with properties exhibited by blends and solutions of the individual oligomers and fullerenes will provide insight into the quenching mechanism.

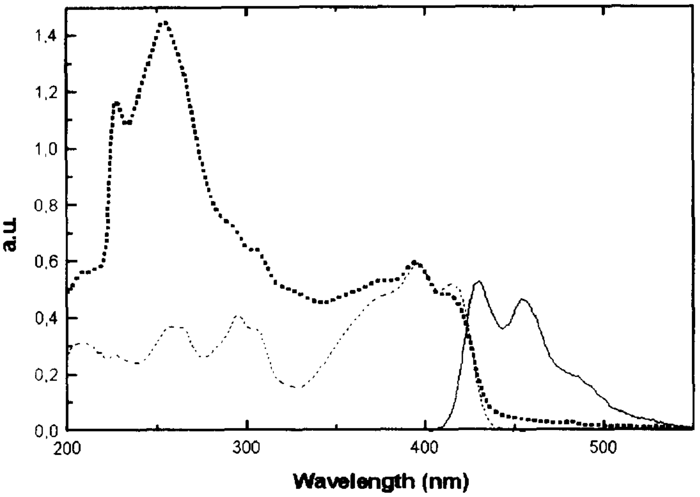


Figure 2. UV-Visible absorption (dashed line) and PL (solid line) spectrum of trimer **2** together with the UV-Vis absorption (dotted line) of triad **3**. Spectra were measured in dichloromethane at room temperature

Acknowledgments. Financial support from the Universidad Complutense de Madrid (Project PR49/98-7805) and DGICYT (Grant PB95-0428-CO2) is gratefully acknowledged. The authors appreciate the cooperation of Prof. G. Orellana in the use of the fluorimeter.

References.

[1] Saricifti NS, Smilowitz L, Heeger AJ, Wudl F. Science 1992; 258: 1474.
[2] Yu G, Gao J, Hummelen JC, Wudl F, Heeger AJ Science 1995; 270: 1789.
[3] Janssen RAJ, Christians MPT, Pakbaz K, Moses D, Hummelen JC, Saricifti NS. J. Chem. Phys. 1994; 102: 2628.
[4] Jannsen RAJ, Hummelen JC, Lee K, Pakbaz K, Saricifti N S, Heeger A J, Wudl, F J. Chem. Phys. 1995; 270: 1789.
[5] Kraabel B, Hummelen JC, Vacar D, Moses D, Saricifti N S, Heeger AJ, Wudl F. J. Chem. Phys. 1996; 104: 4267.
[6] Martín N, Sánchez L, Illescas B., Pérez I. Chem. Rev. 1998; 98: 2527.
[7] Imahori H, Sakata Y, Adv. Mater. 1997; 9: 537.
[8] Janssen RA J., van Hal, PA, Knol, J, Hummelen, JK. communication presented to the European Conference on Organic solar cells ,*ECOS, Cadarache (France)* 1998.
[9] Müllen, K; Wegner, G. Electronic Materials: The Oligomer Approach,. Wiley-VCH, 1998.
[10] For a review see: Roncali J. Chem. Rev. 1997; 97: 173.
[11] Audebert P, Catel JM, Le Costumer G, Duchenet V, Hapiot P. J. Phys. Chem. 1998; 102: 8661.
[12] Effenberger F, Grube G. Synthesis 1998: 1372.
[13] Maggini M, Scorrano G, Prato M. J. Am. Chem. Soc. 1993: 115; 9798.
[14] Prato M, Maggini M. Acc. Chem. Res. 1998; 31: 519
[15] de Lucas A I, Martín N, Sánchez L, Seoane C. Tetrahedron Lett. 1996; 37: 9391.
[16] Higashida S, Imahori H, Kaneda T, Sakata Y. Chem. Lett. 1998: 605.
[17] Fabre TS, Treleaven WD, McCarley TD, Newton CL, Landry RM; Saraiva MC, Strongin R M. J. Org. Chem. 1998; 63: 3522.
[18]Iwasa Y. Tanoue K, Mitani T, Izuoka A, Sugawara T, Yagi T. Chem. Commun. 1998: 1411.
[19] Segura JL, Martin N, Hanack M. Eur. J. Org. Chem. (in press).
[20] Suzuki T, Maruyama Y, Akasaba T, Ando W, Kobayashi K, Nagase S J. Am. Chem. Soc. 1994; 116: 1359.
[21] Echegoyen L, Echegoyen L E, Acc. Chem. Res. 1998; 31: 593.