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# New Chiral Binaphthyl Building Blocks: Synthesis of the First Optically Active Tetrathiafulvalene and 11,11,12,12-Tetracyano-9,10-anthraquinodimethane Dimers[†]

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New enantiomerically pure binaphthyl derivatives bearing triphenylphosphine or phosphonate groups have been synthesized and used as building blocks to prepare the first optically active TTF and TCAQ dimers. Due to the restricted rotation of the two naphthalene rings, binaphthyl derivatives are ideal candidates to be used as nonplanar spacers between electroactive units in the search for materials with enhanced dimensionality. The electronic absorption spectra of dimers in which the electroactive unit is in conjugation with the naphthalene fragment reveal the presence of intramolecular photoinduced electron-transfer process from the TTF to the naphthalene unit in **5** and **6** and from the naphthalene moiety to the TCAQ unit in **7**. Electrochemical studies on the new dimers show the redox potentials of TTF and TCAQ units as well as the oxidation wave for the naphthalene moiety and reveal no significant electronic interaction between the two electroactive units, which is in agreement with the results obtained from theoretical calculations at the PM-3 level which indicate that the angle between rings in the binaphthyl systems ranges from 75 to 80°.

## Introduction

The important role of functionalized 1,1′-binaphthyl with very high enantiomeric purity for the development of chiral materials has been widely recognized.[1] By appropriate functionalization of the 1,1′-binaphthyl core, this moiety has been incorporated in more complex systems with applications in areas such as asymmetric catalysis,[2] molecular recognition,[3] nonlinear optics[4] or photoluminescence.[5] Furthermore, difunctionalized binaphthyl derivatives have been effectively used as comonomers for the synthesis of intrinsically chiral polymeric systems.[1,6] Therefore, the synthesis of new binaphthyl derivatives endowed with reactive functional groups is of importance for the development of new organic materials. In this paper, we report the functionalization of enantiomerically pure binaphthyl systems with new triphenylphosphine (**1**) and phosphonate (**2**) groups, as well as their hydroxymethyl (**3**) and bromomethyl (**4**) substituted precursors (Figure 1). These new substitution patterns open the way to the Wittig[7] and Wittig−Horner[8] olefination reactions, in addition to the Williamson[9] and esterification[10] reactions for the preparation of unsymmetrical ethers and esters, respectively, thus acting as

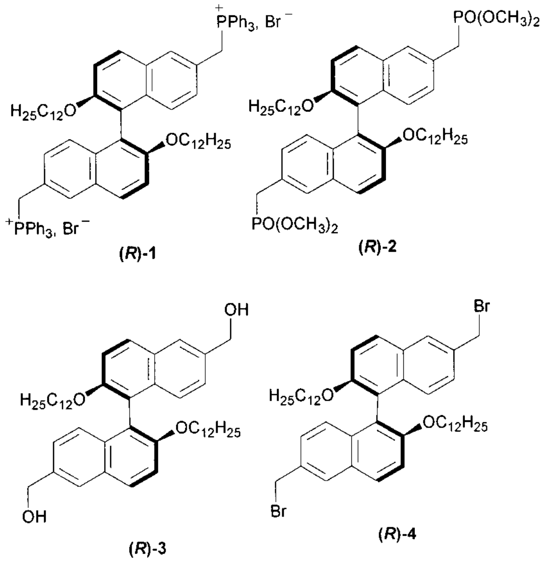

**Figure 1.** New functionalized enanthiomerically pure binaphthyl derivatives.

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[†] This work is dedicated to Prof. José Barluenga on the occasion of his 60th birthday.

(1) Pu, L. *Chem. Rev.* **1998**, *98*, 2405.

(2) (a) Terada, M.; Mikami, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2391. (b) Sasai, H.; Tokunaga, T.; Watanabe, S.; Suzuki, T.; Itoh, N.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 7388. (c) Hu, Q.-S.; Huang, W.-S.; Pu, L. *J. Org. Chem.* **1998**, *63*, 2798. (d) Xiao, D.; Zhang, Z.; Zhang, X. *Org. Lett.* **1999**, *1*, 1679. (e) Pu, L. *Chem. Eur. J.* **1999**, *5*, 2227. (f) Yu, H.-B.; Zheng, X.-F.; Lin, Z.-M.; Hu, Q.-S.; Huang, W.-S.; Pu, L. *J. Org. Chem.* **1999**, *64*, 8149.

(3) (a) Lustenberger, P.; Martinborough, E.; Denti, T. M.; Diederich, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 747. (b) Rusin, O.; Král, V. *Chem. Commun.* **1999**, 2367.

(4) (a) Wong, M. S.; Nicoud, J.-F. *J. Chem. Soc. Chem. Commun.* **1994**, 249. (b) Deussen, H.-J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjornholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841. (c) Deussen, H.-J.; Boutton, C.; Thorup, N.; Geisler, T.; Hendrickx, E.; Bechgaard, K.; Persoons, A.; Bjornholm, T. *Chem. Eur. J.* **1998**, *4*, 240. (d) Verbiest, T.; Kauranen, M.; Persoons, A. *J. Mater. Chem.* **1999**, *9*, 2005.

(5) (a) Gómez, R.; Segura, J. L.; Martín, N. *Chem. Commun.* **1999**, 619. (b) Musick, K. Y.; Hu, Q.-S.; Pu, L. *Macromolecules* **1998**, *31*, 2933.

(6) (a) Pu, L. *Acta Polym.* **1997**, *48*, 116. (b) Gómez, R.; Segura, J. L.; Martín, N. *J. Org. Chem.*, in press. (c) Cheng, H.; Pu, L. *Macromol. Chem. Phys.* **1999**, *200*, 1274.

(7) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

(8) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87.

(9) Feuer, H.; Hooz, J. In *The Chemistry of the ether linkage*; Patai, Ed.; Wiley: New York, 1967; pp 454−466.

(10) Haslam, E. *Tetrahedron* **1980**, *36*, 2409.

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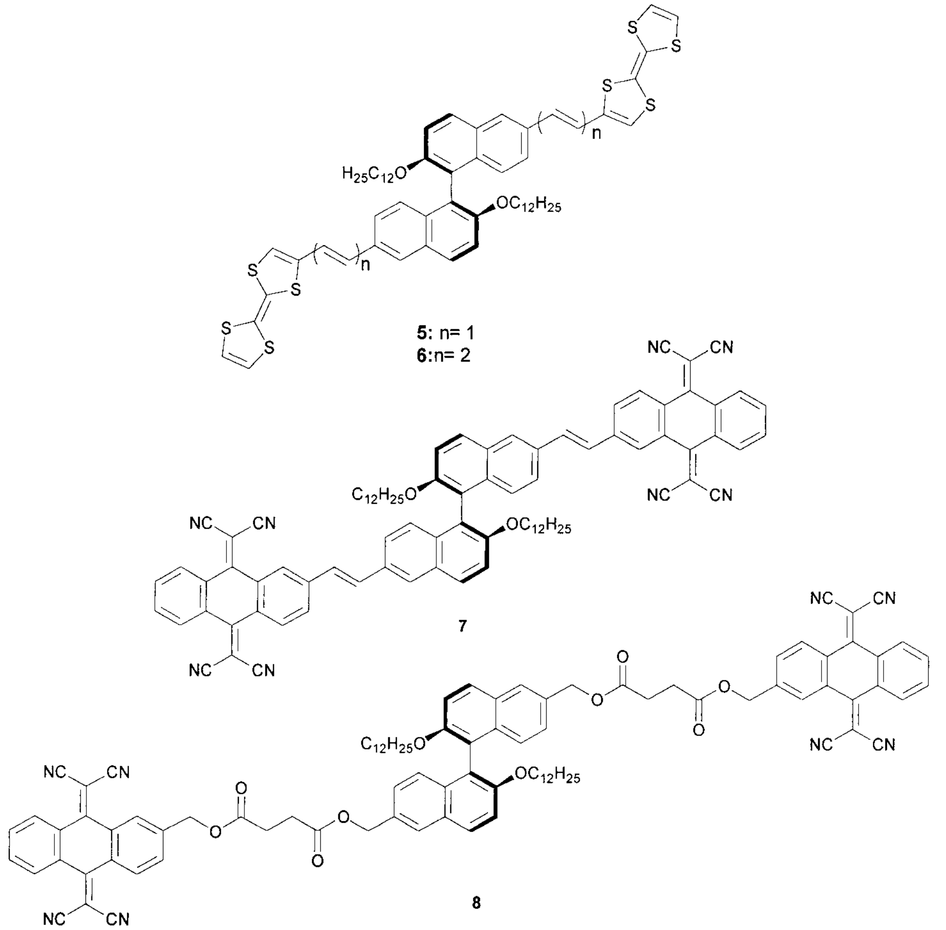


**5:** n= 1
**6:**n= 2

**7**

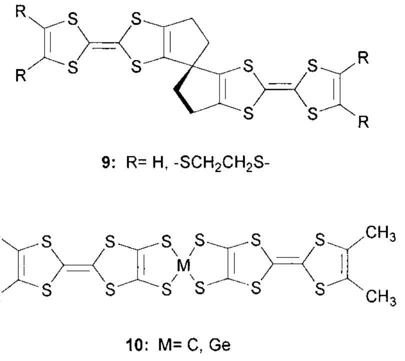
**8**

**Figure 2.** New TTF (**5**, **6**) and TCAQ (**7**, **8**) dimers.

versatile building blocks to be incorporated into a variety of molecular and polymeric materials.

The reactivity of the new binaphthyl derivatives has been tested by reaction with suitably functionalized strong electron donor tetrathiafulvalene (TTF) and strong electron acceptor 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) systems. Thus, the new chiral TTF (**5**, **6**) and TCAQ (**7**, **8**) dimers depicted in Figure 2 have been prepared.

The increase of dimensionality has been identified as a priority in TTF and tetracyano-*p*-quinodimethane (TCNQ) chemistry in order to obtain improved electrically conducting materials. For this purpose, different strategies have been followed.[11,12] The introduction of heavy atoms at peripheral positions of the electroactive moieties or the functionalization of these systems with OH or NHR groups that enable intermolecular hydrogen bonding can be considered as classical methods of achieving a different donor packing motif in charge transfer (CT) complexes and/or salts. The concept of "crystal engineering" proposed by Desiraju[13] has also been applied in the field of molecular conductors to construct supramolecular assemblies.



**9:** R= H, $-SCH_2CH_2S-$

**10:** M= C, Ge

**Figure 3.** Dimeric TTF dimers with spiro linkage.

Although much less explored, a promising strategy involves the design of nonplanar materials[14] and the use of spiroconjugation[15] as a way to add dimensionality in the design of organic materials. For example, dimeric systems (**9**,[16] **10**,[17] Figure 3) where the two TTF units are connected through a spiro linkage are able to form a two-dimensional column and $\pi$- and/or $\sigma$-interactions.

In this paper, we use the above functionalized chiral binaphthyl units as a new approach for obtaining the first examples of TTF[18] (**5**, **6**) and TCAQ (**7**, **8**) chiral dimers

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[11] Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481.

[12] (a) Martín, N.; Segura, J. L.; Seoane, C. *J. Mater. Chem.* **1997**, *7*, 1661. (b) Martín, N.; Seoane, C. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, 1997; Vol. 1, Chapter 1.

[13] (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (b) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (c) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375.

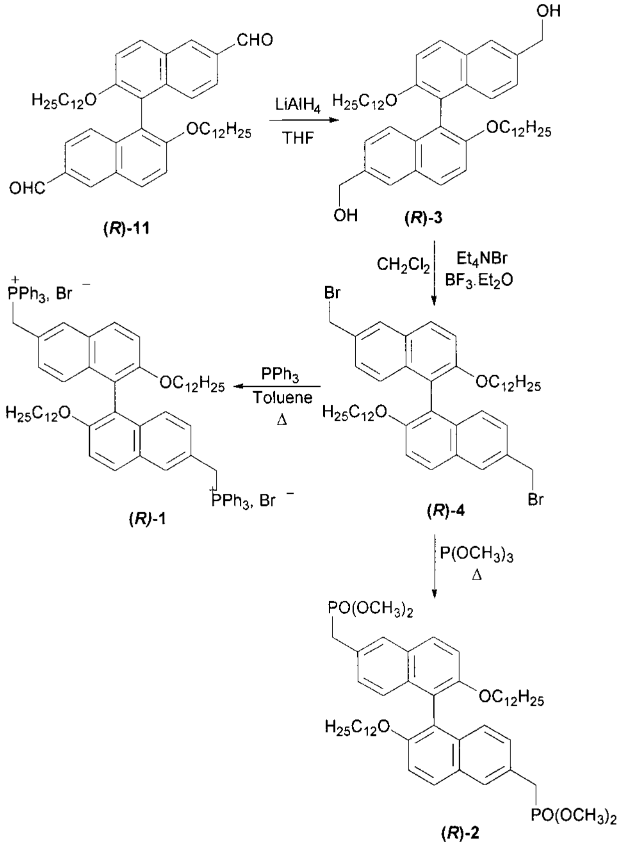
[14] (a) Kato, H.; Kobayashi, T. *Adv. Mater.* **1993**, *98*, 1375.

[15] Maslak, P. *Adv. Mater.* **1994**, *6*, 405.

[16] Tatemitsu, H.; Nishikawa, E.; Sakata, H.; Misumi, S. *Synth. Met.* **1987**, *19*, 565.

[17] Ueda, K.; Yamanoha, M.; Sugimoto, T.; Fujita, H.; Ugawa, A.; Yakushi, K.; Kano, K. *Chem. Lett.* **1997**, 461.

**Scheme 1**

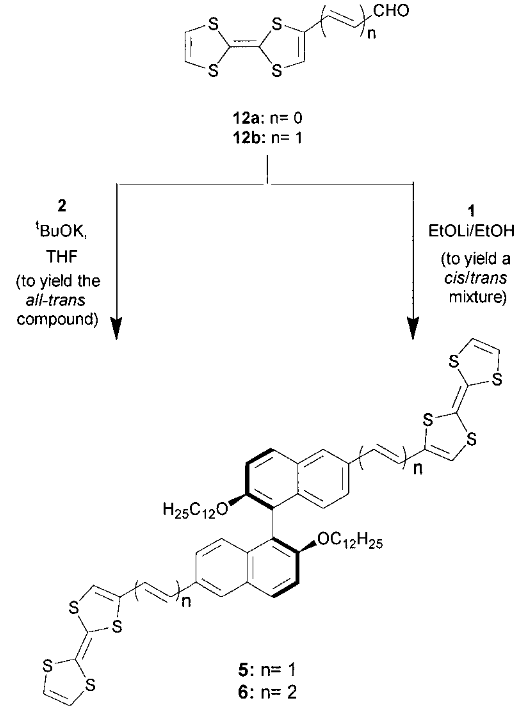


in the search for enhanced dimensionality. Due to the restricted rotation of the two naphthalene units of the binaphthyl system, the dihedral angle between rings ranges from 60° to 120°, and therefore, these binaphthyl derivatives are ideal candidates to be used as nonplanar spacers connecting electroactive fragments. The electrochemical properties of the new electroactive chiral dimers have been studied by cyclic voltammetry in solution and their structural properties determined by theoretical calculations at the semiempirical PM3 level.

## Synthesis

**1. Synthesis of Functionalized Binaphthyl Derivatives.** The synthesis of appropriately functionalized binaphthyl derivatives is depicted in Scheme 1. The resolution of the (±)-1,1′-bi-2-naphthol was carried out by using (−)-*N*-benzylzinconidinium chloride as the chiral resolution reagent,[19] and the enantiomerically pure *R* isomer was used in the subsequent reactions. (*R*)-2,2′-Didodecyloxy-6,6′-diformyl-1,1′-binaphthyl (**11**) was obtained by using the three-step reaction sequence recently reported by our group.[5] The presence of long alkyl chains on the binaphthyl unit is important in order to enhance the solubility of the final dimeric materials. (*R*)-Bis(hydroxymethyl) derivative **3** was obtained upon reduction of **11** with lithium aluminum hydride in dry THF. Further treatment of **3** with tetraethylammonium bromide and boron trifluoride etherate in dry dichloromethane[20] afforded the (*R*)-bis(bromomethyl) derivative **4**. (*R*)-Bisphosphonium dibromide (**1**) was obtained from **4** by treatment with triphenylphosphine in refluxing toluene. (*R*)-Bisphosphonate (**2**) could be similarly obtained from **4** upon heating in trimethyl phosphite followed by chromatographic purification (Scheme 1).

**Scheme 2**



The structure of the compounds prepared was ascertained by using spectroscopic (FT-IR, $^1H$ NMR, $^{13}C$ NMR, mass spectrometry) and elemental analysis procedures. As the binaphthyl derivatives have been synthesized by using enantiomerically pure starting materials, they have been obtained with the following optical rotations ($[\alpha]_D$): −42.14 (*c* 1.4 × $10^{-3}$, $CHCl_3$) for (*R*)-**1**, +19.14 (*c* 3.5 × $10^{-3}$, $CHCl_3$) for (*R*)-**2**, +21.67 (*c* 1.2 × $10^{-3}$, $CHCl_3$) for (*R*)-**3**, and −12.72 (*c* 2.2 × $10^{-3}$, $CHCl_3$) for (*R*)-**4**.

**2. Synthesis of TTF and TCAQ Dimers.** Recent structural and electronic modifications of TTF place emphasis on the preparation of dimeric TTF[21] molecules and higher oligomers,[22] in which the TTF units are linked by one or more spacer groups. Such electron donor systems might have intramolecular through-bond or through-space interactions between the TTF units and accordingly display multistage redox behavior, which affects the formation, structure, and physical properties of their charge transfer (CT) complexes and radical salts. In other words, dimeric and oligomeric TTF derivatives might provide an opportunity to control the stoichiometry, band filling, and molecular assembly in desired conductive complexes.

TTF dimers **5** and **6** were obtained by using both Wittig and Wittig−Horner reactions (Scheme 2). When a mixture of bis(triphenylphosphonium) salt **1** and formyl-TTF (**12a**)[23] in dry ethanol was heated at 50 °C for 90 min

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[18] Gómez, R.; Segura, J. L.; Martín, N. *Org. Lett.* **2000**, *2*, 1585.

[19] Hu, Q. S.; Vitharama, D.; Pu, L. *Tetrahedron*: *Asymmetry* **1995**, *6*, 2123.

[20] Mandal, A. K.; Mahajan, S. W. *Tetrahedron Lett.* **1985**, *26*, 3863.

[21] Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater.* **1996**, *8*, 203.

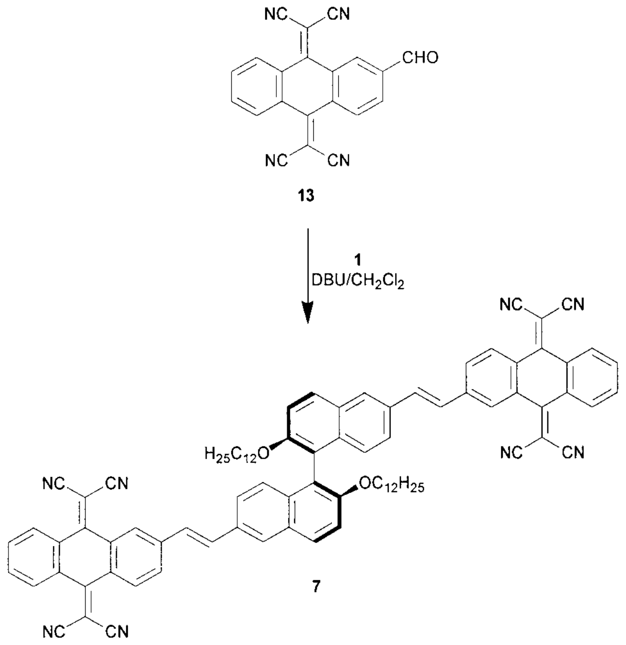
[22] (a) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439. (b) Becher, J.; Lau, J.; Mørk, P. In *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: New York, 1998; pp 198−233.

[23] Garín, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 490.

using lithium ethoxide as a base, dimer **5** was isolated in a 69% yield as a mixture of *cis*/*trans* isomers. $^1$H NMR spectroscopy showed that the major compound was the *all-trans* derivative ($J_{\text{trans}} = 15.9$ Hz) and less than 10% of the *all-cis* derivative ($J_{\text{cis}} = 12.0$ Hz) could be observed. However, we were not able to separate both isomers chromatographically. Attempts at cis/trans isomerization by heating a toluene solution of **5** in the presence of iodine produced a dark mixture due, probably, to the formation of the radical-ion salt of the TTF derivative.

As an alternative to the above Wittig reaction, for a better control on the stereochemical outcome of the olefination reaction, we performed Wittig–Horner reactions between phosphonate **2** and formyl-TTF **12a** and its vinylogue **12b**.[24] To a solution of **2** and the corresponding formyl-TTF **12** in dry THF was added potassium *tert*-butoxide, and the mixture was stirred at room temperature for 1.5 h. After extraction of the reaction crude with methylene dichloride, the solvent was removed under vacuum and the residue was chromatographed to yield TTF dimer **5** and its vinylogue **6** as stable red solids. Although lower yields were obtained (around 15%) for the TTF dimers, Wittig–Horner reactions afforded solely the *all-trans* configuration product. The presence of the long alkyl chains on the binaphthyl moiety resulted in highly soluble TTF dimers, which allow spectroscopic and electrochemical characterization. The observed optical rotations ($[\alpha]_D$) are $-221.2$ ($c = 3.3 \times 10^{-4}$, $CHCl_3$) for (*R*)-**5** and $-587.9$ ($c = 3.3 \times 10^{-4}$, $CHCl_3$) for (*R*)-**6**.

**Scheme 3**



Electron acceptor molecules containing more than one TCNQ moiety have been almost neglected probably due to the difficulties found in the functionalization of the TCNQ system in comparison with the rich chemistry of the TTF molecule.[12a] Thus, only a few examples of multiTCNQ molecules are known.[25] One of the most interesting aspects in the synthesis of TCNQ derivatives has been to increase the $\pi$-extension of the electron acceptors in order to decrease the intramolecular Coulomb repulsion, resulting in more stable radical dianions.[26] We have recently described the synthesis of 2-formyl-11,11,12,12-tetracyano-9,10-anthraquinodimethane (**13**),[27] a $\pi$-extended TCNQ analogue that is suitably functionalized to be incorporated into more complex systems[28] through, among others, Wittig or Wittig–Horner reactions. On the other hand, Panetta and co-workers have reported the synthesis of the 2-hydroxymethyl-11,11,12,12-tetracyano-9,10-anthraquinodimethane (**14**) in order to incorporate the TCAQ acceptor moiety in organic rectifiers.[29] These readily available TCNQ derivatives (**13**, **14**) are suitable starting materials for the preparation of chiral dimeric acceptors by further reaction with the appropriately functionalized 1,1′-binaphthyl derivatives.

When a mixture of bis(triphenylphosphonium) salt (*R*)-**1** and 2-formyl-11,11,12,12-tetracyano-9,10-anthraquinodimethane (**13**) in dry dichloromethane at 0 °C using 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base was used, dimer (*R*)-**7** was isolated in a 60% yield as a mixture of *cis*/*trans* isomers from which the *all-trans* isomer could be separated chromatographically (Scheme 3). In contrast to the above TTF dimers, the reaction was carried out in dichloromethane instead of ethanol due to the lack of solubility of the TCAQ derivative in ethanol. Furthermore, due to the strong sensitivity of the TCAQ moiety to strong bases, it was necessary to carry out the reaction at 0 °C and using the weak base DBU. Iodine-catalyzed thermal isomerization of the mixture did not take place and the need of stronger bases to carry out the Wittig–Horner reaction prevented us for obtaining exclusively the pure *all-trans* or *all-cis* derivatives.

As an alternative for the synthesis of chiral TCAQ dimers we used 2-hydroxymethyl-11,11,12,12-tetracyano-9,10-anthraquinodimethane (**14**) as the starting material. By reaction of **14** with succinic anhydride (**15**) in dichloromethane in the presence of 4-(dimethylamino)pyridine and pyridine, a TCAQ derivative endowed with a carboxylic acid functional group (**16**) was obtained. Reaction of bis(hydroxymethyl)substituted binaphthyl derivative (*R*)-**3** with functionalized TCAQ **16** in dry chloroform in the presence of 1,3-dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine afforded the TCAQ dimer (*R*)-**8** as an orange solid in 44% yield. A pure sample of this compound could be obtained by chromatographic purification of the crude compound (Scheme 4).

## Electronic Absorption Spectra

The influence of the donor and acceptor ability of TTF

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[24] González, M.; Martín, N.; Segura, J. L.; Garín, J.; Orduna, J. *Tetrahedron Lett.* **1998**, *39*, 3269.

[25] (a) Mitsuhashi, T.; Goto, M.; Honda, K.; Maruyama, Y.; Sugaware, T.; Inabe, T.; Watanabe, T. *J. Chem. Soc. Chem. Commun.* **1987**, 810. (b) Mitsuhashi, T.; Goto, M.; Honda, K.; Maruyama, Y.; Sugaware, T.; Inabe, T.; Watanabe, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 261. (c) Fukushima, T.; Okazeri, N.; Miyashi, T.; Suzuki, Y.; Yamashita, Y.; Suzuki, T. *Tetrahedron Lett.* **1999**, *40*, 1175. (d) Takahashi, K.; Kobayashi, K. *Tetrahedron Lett.* **1999**, *40*, 5349.

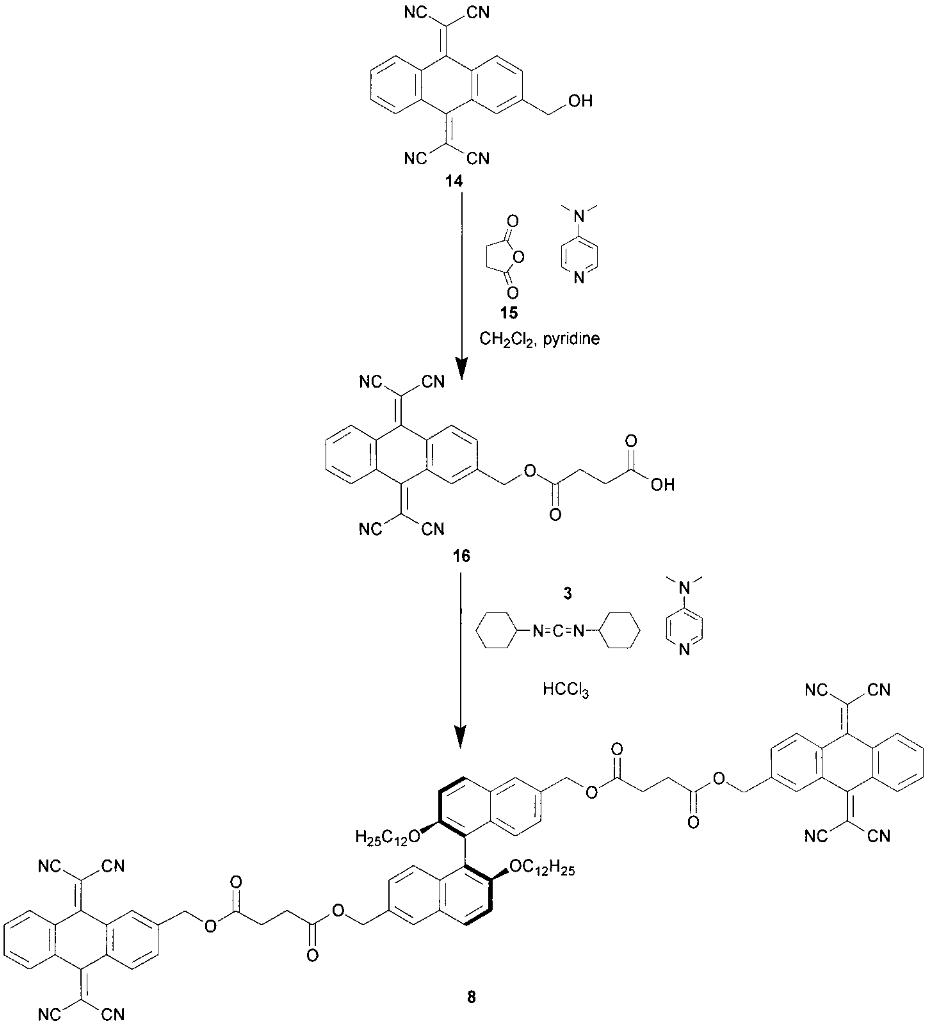
[26] (a) Martín, N.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1522. (b) Martín, N.; Behnisch, R.; Hanack, M. *J. Org. Chem.* **1989**, *54*, 2563. (c) Suzuki, T.; Fujii, H.; Yamashita, Y.; Kabuto, C.; Tanaka, S.; Harasawa, M.; Mukai, T.; Miyashi, T. *J. Am. Chem. Soc.* **1992**, *114*, 3034. (d) Martín, N.; Segura, J. L.; Seoane, C. *J. Org. Chem.* **1995**, *60*, 4077. (e) Ortí, E.; Viruela, R.; Viruela, P. M. *J. Mater. Chem.* **1995**, *5*, 1697.

[27] Illescas, B.; Martín, N.; Seoane, C. *Tetrahedron Lett.* **1997**, *38*, 2015.

[28] Zerza, G.; Scharber, M. C.; Brabec, C. J.; Sariciftci, N. S.; Gómez, R.; Segura, J. L.; Martín, N.; Srdanov, V. I. *J. Phys. Chem. A* **2000**, *104*, 8315.

[29] Panetta, C. A.; Heimer, N. E.; Hussey, C. L.; Metzger, R. M. *Synlett* **1991**, 301.

**Scheme 4**



and TCAQ moieties respectively can be clearly distinguished in the electronic spectra of the new dimers. While didocecyloxybinaphthalene presents absorption maximum at 344 nm and TTF and vinyl-TTF at 370 and 391 nm, respectively, dimer **5** exhibits a maximum at 432 nm and **6** at 450 nm. This band could be accounted for by the HOMO−LUMO transition of the whole conjugated system comprising the TTF moiety and the vinylnaphthalene unit. Due to the longer conjugated system in **6** with respect to dimer **5**, the absorption maxima is shifted to longer wavelengths for **6**. Similar charge-transfer absorption from the HOMO, which is located on the TTF moiety, to the LUMO, which spreads on the naphthalene unit, have been recently reported in naphthalene containing largely $\pi$-extended TTF derivatives.[30]

As a consequence of the acceptor nature of the TCAQ moiety and the donor nature of the alkoxynaphthalene unit, a different pattern was observed in the UV−vis spectra of the TCAQ dimers **7** and **8**. Binaphthyl derivatives bearing acceptor groups such as nitriles or dicyanovinylenes have been previously reported to exhibit second-order nonlinear optical (NLO) properties due to the donor ability of the alkoxynaphthalene system.[4] It is well-known that conjugated donor−acceptor substituted organic molecules have high molecular hyperpolarizabilities ($\beta$). One common feature of these materials is the presence of a low energy absorption band in the electronic spectra, which is assigned to an intramolecular charge transfer (ICT) given that the HOMO of these systems is mainly located on the donor part of the molecule while the LUMO is located on the acceptor part. Thus, dimer **7** in which the donor alkoxynaphthalene unit is linked through a conjugated vinylene bridge to the acceptor TCAQ moiety exhibits an absorption maxima at 510 nm (Figure 4) that is clearly red shifted in comparison with the absorption bands observed for the binaphthyl (370 nm) and the TCAQ (342 nm) systems. Considering the good NLO properties reported for other binaphthyl-based materials endowed with weak acceptor groups, it is expected that dimer **7** could find a realistic and outstanding application in this field. Work is in progress in order to study the potential of these TCAQ derivatives in this area.

No low energy absorption band was observed in the electronic spectra of dimer **8** due to the lack of conjugation between the dodecyloxynaphthalene unit and the TCAQ moiety. For this compound, the electronic spectra is a simple superimposition of the spectra of the isolated moieties indicating that no through bond or space interaction between both moieties takes place in the ground state (Figure 4).

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[30] Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela, P. N.; Viruela, R. *J. Org. Chem.*, **1998**, *63*, 1268.

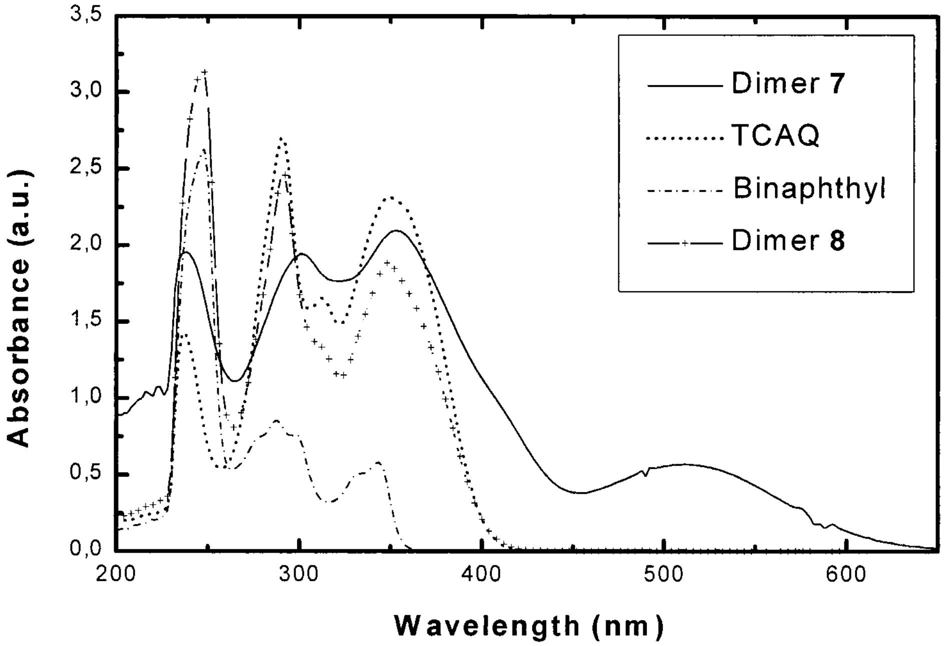


**Figure 4.** UV−vis spectra for dimers **7** and **8**, TCAQ and binaphthyl.

## Electrochemistry

The redox properties of the novel electroactive compounds **5**−**8** were determined by cyclic voltammetry (CV) measurements at room temperature in dichloromethane as solvent, using a GCE (glassy carbon) as working electrode, SCE as reference electrode, and $Bu_4N^+ClO_4^-$ as supporting electrolyte.

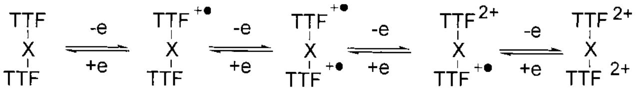
Different degrees of electronic interaction between the TTF units have been observed in previous examples of TTF dimers depending upon the geometry of the molecule and the nature of the spacer connecting the TTF units.[21] As these molecules contain two redox-active moieties, they are able to form up to the tetracation, because each TTF unit can release two electrons (Scheme 5).

The cyclic voltammetry of both TTF dimers **5** and **6** show two quasireversible redox waves, each of them involving a two-electron process ($E^1_{ox} = 0.525$ V and $E^2_{ox} = 0.905$ V for **5** and $E^1_{ox} = 0.440$ V and $E^2_{ox} = 0.835$ V for **6**, compared with $E^1_{ox,1/2} = 0.372$ V and $E^2_{ox,1/2} = 0.672$ V for the parent TTF under the same conditions). Similarly to other nonconjugated TTF dimers, the electrochemical redox properties of these dimers (**5**, **6**) correspond with the formation of the respective dication and tetracation, with no intermediate oxidation states detected. These findings suggest that there is no Coulombic repulsion effects between charged TTF moieties and that the individual TTF units are electronically isolated by the binaphthyl spacer and do not interact to any significant extent.

A third oxidation wave, corresponding to the naphthalenevinylene moieties, appears at 1.655 V for **5** and at 1.425 V for **6**. The less positive value of the third oxidation wave observed for **6** in comparison with that observed for **5** may be due to the inclusion of an additional vinylene unit which extends the $\pi$-conjugation making the system more easily oxidizable.

Concerning the CV measurements of the TCAQ dimers, only a quasireversible reduction wave involving four electrons could be observed ($E^1_{red} = -0.410$ V for **7** and $E^1_{red} = -0.416$ V for **8** in comparison with $E^1_{red} = -0.375$ V for TCAQ) (Figure 5). In contrast to TCNQ that presents two reduction waves to the radical anion ($TCNQ^{\bullet-}$) and dianion ($TCNQ^{2-}$), TCAQ derivatives present a single-wave reduction involving two electrons corresponding to an overall process leading to the dianion ($TCAQ^{2-}$). The presence of a single reduction wave in the TCAQ dimers (**7**, **8**) suggests that both TCAQ units are simultaneously oxidized to the tetraanion, indicating that the individual TCAQ units are electronically isolated by the binaphthyl spacer and do not interact electronically to any significant extent.

**Scheme 5**



In addition to the reduction wave, the cyclic voltammograms of the TCAQ dimers show an oxidation wave at $E^1_{ox} = 1.380$ V for **7** and at $E^1_{ox} = 1.469$ V for **8**. This oxidation wave can be reasonably assigned to the oxidation of the alkoxynaphthalene moiety while the oxidation process observed for **7** should involve to the naphthalenevinylene system.

## Structural Study

To gain an insight into the structure of the dimers synthesized as well as to rationalize the above-described UV−vis spectra and electrochemical data, we have calculated the optimized geometries of models of the TTF and TCAQ dimers presented in this paper using the semiempirical PM3 method as implemented in the Hyperchem 3.0 system of programs. The PM3 method is reparametrization of the MNDO approach[31] in which the AM1 form of the core−core interaction is used.[32] Compared to MNDO, the PM3 technique provides a much improved description of the interactions taking place

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(31) Dewar, M: S. J.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(32) Dewar, M: S. J.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

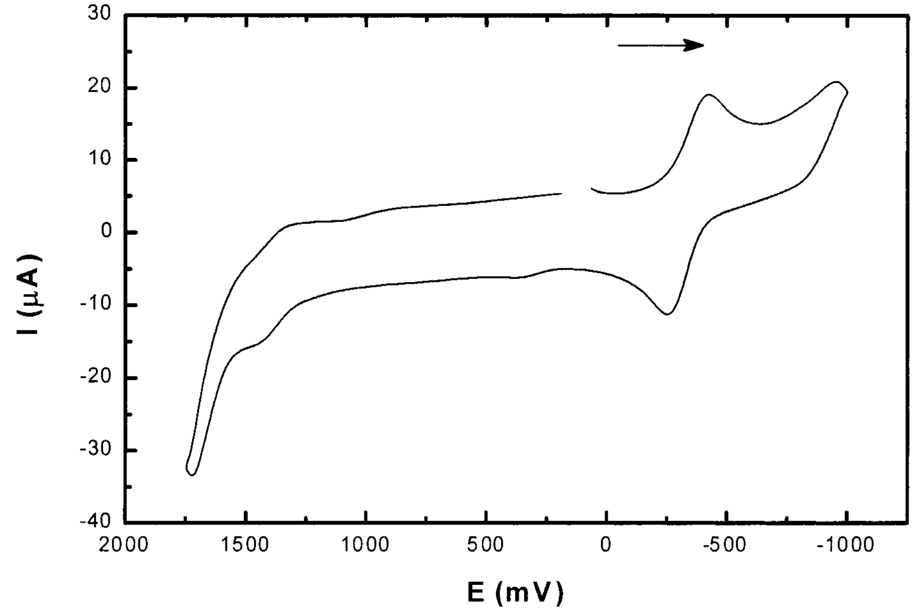

**Figure 5.** Cyclic voltammograms for TCAQ dimer **8**.

between nonbonded atoms, *e.g.*, hydrogen bonding or steric interactions.[33] The latter are specially important for the binaphthyl and TCAQ derivatives since they determine the nonplanarity of the systems.

In agreement with previous bibliographic references, a torsion angle of 78.25° is observed for the binaphthyl moiety (see Figure S1 in Supporting Information). On the other hand, an almost planar system is observed for the tetrathiafulvalenyl-naphthalenevinylene moiety which is in agreement with the observation of a red shift in the absorption of this system in comparison with that observed for isolated binaphthyl or TTF. On the other hand, the lack of interaction between the TTF units in the dimers can be justified by the almost perpendicular geometry observed for the binaphthyl moiety which interrupts the extension of the conjugated system. The lack of through-bond interactions between both TTF units suggests that they must behave independently in further complexation reactions.

A torsion angle of 76.1° is observed for the binaphthyl system of the *all-trans* isomer of the model compound of TCAQ dimer **7** (Figure S2 in the Supporting Information). Similarly to the above-mentioned model of TTF, the dodecyloxy chain has been replaced by a methoxy group to facilitate calculations. Torsion angles close to 0° are measured for the TCAQ-naphthalenevinylene systems which is in agreement with the charge-transfer band observed in the UV−vis spectra correponding to a conjugated donor−$\pi$-acceptor system. As has been previoulsy reported,[26d,34,35] the TCAQ moiety adopts a nonplanar structure due to the strong steric interactions that take place between the cyano groups and the hydrogens in peri positions.

Due to the lack of through-bond interaction between the TCAQ moieties as a consequence of the perpendicular geometry imparted by the binaphthyl moiety which effectively interrupts the conjugation, both electroactive moieties accept two electrons simultaneously to form the tetraanion.

The almost perpendicular conformation observed for the electroactive components of the binaphthyl derivatives and the good donor and acceptor abilities exhibited respectively by the TTF and TCAQ dimers will make them ideal candidates for the preparation of charge-transfer complexes and salts with unique three-dimensional arrangements.

## Summary

In summary, we have developed a general synthetic route for the preparation of optically active TTF and TCAQ dimers containing binaphthyl units. The synthesis of binaphthyl derivatives bifunctionalized with either triphenylphosphine, phosphonate, hydroxymethyl, and bromomethyl groups will allow to extend this synthetic route to many other electroactive dimers with enhanced dimensionality and even to different conjugated−nonconjugated block copolymers.

Due to the perpendicular conformation observed for the binaphthyl core, no electronic interactions between the electroactive units in the dimers are observed. Thus, the individual TCAQ and TTF units in the chiral dimers are electronically isolated by the binaphthyl spacer and do not interact to any significant extent, which strongly suggests that they will behave independently in complexation reactions. This finding, together with the good donor and acceptor ability exhibited respectively by the TTF and TCAQ derivatives and the perpendicular conformation of the binaphthyl system will make them ideal candidates for the preparation of charge-transfer complexes and salts with unique three-dimensional arrangements.

Apart from the potential of these materials as precursors for charge-transfer complexes and salts, other interesting applications for some of these compounds can be envisaged. Considering the good NLO properties

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[33] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209; 221.

[34] Viruela, R.; Viruela, P. M.; Ortí, E.; Martín, N. *Synth. Met.* **1995**, *70*, 1031.

[35] (a) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618. (b) Schubert, U.; Hünig, S.; Aumüller, A. *Liebigs Ann. Chem.* **1985**, 1216. (c) Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 506.

reported for binahthyl-based materials endowed with weak acceptor groups, the observation of a charge-transfer band in the UV–vis spectra of dimer **7** as a consequence of the D–$\pi$–A system formed by the alkoxynaphthalene–vinylene–TCAQ system, the dimers now reported could find application in this field.

Finally, we have recently reported the fabrication of photovoltaic devices in which the active layer are formed by blends of soluble TCAQ derivatives together with conjugated polymers.[36] Although efficient photoinduced charge transfer has been observed for TCAQ-conjugated polymer blends,[37] phase segregation takes place due to the different natures of the molecular and polymeric materials. We have also reported the synthesis of binaphthyl-based luminescent conjugated–nonconjugated block copolymers with efficient photoinduced charge-transfer for photovoltaic devices. Thus, TCAQ dimer **8** containing not only the long dodecyloxy chains but also the ester-type spacers and the binaphthyl unit will be an ideal candidate to prepare blends with the binaphthyl-based polymers. The similarity between the structures of polymers and TCAQ derivatives will probably enhance the miscibility of both species thus decreasing phase segregation which will increase the lifetimes of the charge separated states in this type of photovoltaic devices. Work is currently in progress for the preparation of these appealing molecules

## Experimental Section

All melting points were measured with a melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets or neat films. $^{13}$C and $^{1}$H NMR spectra were recorded with a 300 MHz for $^{1}$H and 75 MHz for $^{13}$C spectrometer. Chemical shifts are given as $\delta$ values (int. Standard: TMS). [$\alpha_D$] values were detemined by using the light of a sodium lamp ($\lambda$ = 589 nm), at room temperature, in a cilindric cell with a length of 1 dm and a volumen of 1 mL. Semiempirical calculations (PM3) were performed using the program Hyperchem (version 3.0) from Hypercube Inc. with a PC compatible at 200 MHz. For each structure the minimum energy was determined after reminimization. Cyclic voltammograms were recorded on a potentiostat/galvanostat equipped with electrochemical analysis software by using a GCE (glassy carbon) as working electrode, SCE as reference electrode, $Bu_4NClO_4$ as supporting electrolyte, dichloromethane as solvent, and at a scan rate of 200 mV/s. (±)-2,2′-Dihydroxy-1,1′-binaphthalene is commercially available and was used without further purification. Pyridine was dried with calcium hydride, chloroform and dichloromethane were distilled from $CaCl_2$, and ethanol was distilled from Mg and iodine.

**Synthesis of Binaphthyl Derivatives. (*R*)-6,6′-Bis(hydroxymethyl)-2,2′-didodecyloxy-1,1′-binaphthalene (3).** To a refluxing solution of 2 g (3.0 mmol) of (*R*)-2,2′-didocecyloxy-6,6′-diformyl-1,1′-binaphthalene (**11**)[5a] in 125 mL of dry THF was added 342 mg (9.0 mmol) of lithium aluminum hydride during 20 min under argon atmosphere. After 2 h, the reaction was allowed to cool at room temperature, and then 200 mL of water was added. The mixture was extracted twice with chloroform, and the combined organic layers were washed with water and then dried over magnesium sulfate. After vacuum removal of the solvent, a yellow oil was obtained that was chromatographed (silica gel, dichloromethane 9.5/methanol 0.5) to yield 1.89 g (93%) of **3** as a colorless oil: $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.88 (d, 2H, $J$ = 8.9 Hz), 7.79 (s, 2H), 7.38 (d, 2H, $J$ = 8.9 Hz), 7.17 (dd, 2H, $J_1$= 8.7, $J_2$= 1.6 Hz), 7.09 (d, 2H, $J$ = 8.7 Hz), 4.75 (s, 4H), 3.95–3.81 (m, 4H), 1.73 (s, 2H), 1.32 (q, 4H, $J$ = 6.9 Hz), 1.17 (s, 20H), 0.91 (m, 16H), 0.81 (t, 6H, $J$ = 6.1 Hz). $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 154.5, 135.5, 133.6, 128.8, 125.8, 125.5, 125.4, 120.4, 115.9, 69.5, 65.4, 31.7, 29.5, 29.3, 29.2, 29.0, 25.5, 22.5, 13.9; FTIR (neat film, cm$^{-1}$) 3338, 3051, 2924, 2853, 1597, 1468, 1273, 1246, 1047; EM *m/z* (EI) (%I) 682 (100), 514 (23), 346 (47), 57 (11). Anal. Calcd for $C_{46}H_{66}O_4$: C, 80.89; H, 9.74. Found: C, 80.60; H, 10.02.

**(*R*)-6,6′-Bis(bromomethyl)-2,2′-didodecyloxy-1,1′-binaphthalene (4).** Under argon atmosphere, 1.75 g (8.3 mmol) of tetraethylammonium bromide and 1.02 mL (8.3 mmol) of boron trifluoride etherate were added dropwise to a solution of 1.89 g (2.8 mmol) of **3** in 20 mL of dry dichloromethane, and the mixture was refluxed during 3 h. After this time the reaction was allowed to reach room temperature and treated with a saturated solution of sodium bicarbonate. The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were washed with a 10 % aqueous solution of sodium bisulfite and then with water. After drying over magnesium sulfate, the organic solvent was removed under vacuum and the oily residue obtained was chromatographed (silica gel, hexane 8/dichloromethane 2) to yield 720 mg (32%) of **4** as a yellow oil: $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.82 (d, 2H, $J$ = 8.9 Hz), 7.76 (d, 2H, $J$ = 1.7 Hz), 7.33 (d, 2H, $J$ = 8.9 Hz), 7.15 (dd, 2H, $J_1$ = 8.8, $J_2$ = 1.7 Hz), 7.03 (d, 2H, $J$ = 8.8 Hz),4.56 (s, 4H), 3.94–3.77 (m, 4H),1.32 (q, 4H, $J$ = 6.8 Hz), 1.17(s, 36H), 0.81 (t, 6H, $J$ = 6.1 Hz); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 155.1, 133.8, 132.3, 129.2, 128.7, 127.9, 126.9, 126.2, 120.2, 115.9, 69.5, 34.4, 31.9, 29.6, 29.4, 29.4, 29.3, 29.2, 29.1, 25.5, 22.6, 14.1; FTIR (neat film, cm$^{-1}$) 2922, 2852, 1595, 1504, 1439, 1275, 1250, 1169; EM *m/z* (EI) (%I) 729 (13), 650 (100), 482 (22), 314 (62), 57 (31). Anal. Calcd For $C_{46}H_{64}Br_2O_4$: C, 68.31; H, 7.97. Found: C, 68.60; H, 8.10.

**(*R*)-[2,2′-Didodecyloxy-6,6′-[1,1′-binaphthylbis(methylene)]]bisphosphonium dibromide (1).** To a solution of 250 mg (0.4 mmol) of **4** in 20 mL of toluene under argon atmosphere was added 546 mg (1.6 mmol) of triphenylphosphine. After the resulting suspension was refluxed during 4 h, the reaction was allowed to cool at room temperature and the solvent was vacuum evaporated. The solid residue obtained was chromatographed (silica gel, dichloromethane 9.5/methanol 0.5) to yield 340 mg (64%) of **1** as a white solid: mp 181–183 °C; $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 7.67–7.42 (m, 32H), 7.22 (d, 2H, $J$ = 9.0 Hz), 6.92 (d, 2H, $J$ = 8.8 Hz), 6.73–6.61 (m, 4H), 5.49 (t, 2H, $J$ = 14.6 Hz), 5.15 (t, 2H, $J$ = 14.6 Hz), 3.97 (t, 4H, $J$ = 6.4 Hz), 1.86 (s, 4H), 1.31–0.97 (m, 36H), 0.80 (t, 6H, $J$ = 6.9 Hz); FTIR (KBr, cm$^{-1}$) 2922, 2851, 1437, 1335, 1248, 1111, 1028; EM *m/z* (ESI) (%I) 1330 (3), 1171 (100), 1003 (24), 946 (85). Anal. Calcd For $C_{82}H_{94}O_2P_2Br_2$: C, 73.87; H, 7.06. Found: C, 72.00; H, 7.03.

**(*R*)-Tetramethyl[2,2′-didodecyloxy-6,6′[1,1′-binaphthylbis(methylene)]]bis-phosphonate (2).** A solution of 630 mg (0.75 mmol) of **4** in 37.5 mL (0.28 mol) of trimethyl phosphite was refluxed for 4 h. After this time, the excess trimethyl phosphite was removed under vacuum to yield a colorless oil which was chromatographed (silica gel, ethyl acetate 9.5/methanol 0.5) to afford 534 mg (82%) of **2** as a colorless oil: $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.81 (d, 2H, $J$ = 9.0 Hz), 7.69 (s, 2H), 7.32 (d, 2H, $J$ = 9.0 Hz), 7.08–6.98 (m, 4H), 3.90 (t, 4H, $J$ = 6.4 Hz), 3.62 (d, 6H, $J$ = 2.6 Hz), 3.56 (d, 6H, $J$ = 2.6 Hz), 3.20 (d, 4H, $J$ = 21.0 Hz), 1.37–0.92 (m, 40H), 0.81 (t, 6H, $J$ = 6.2 Hz); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 154.5, 136.2, 133.8, 129.2, 129.2, 128.8, 127.2, 127.0, 126.8, 125.9, 69.7, 54.4, 54.2, 52.9, 52.2, 52.1, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 25.6, 22.7, 14.1, 11.3, 8.4; FTIR (neat film, cm$^{-1}$) 2955, 2923, 2852, 1597, 1256, 1186, 1035; EM *m/z* (EI) (%I) 698 (16), 530 (100), 421 (35), 311 (32), 265 (24), 57 (55). Anal. Calcd For $C_{50}H_{76}O_8P_2$: C, 69.26; H, 8.77. Found: C, 64.67; H, 8.34.

**Synthesis of Tetrathiafulvalene Dimers. (*R*)-6,6′-Bis-[2″(tetrathiafulvalenyl)vinyl]-2,2′-didodecyloxy-1,1′-binaphthalene (5). Method 1.** Under argon atmosphere, 82 mg of formyltetrathiafulvalene (**12a**) in 7 mL of dry THF and 63 mg (0.56 mmol) of potassium *tert*-butoxide were added

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[36] Zerza, G.; Röthler, B.; Sariciftci, N. S.; Gómez, R.; Segura, J. L.; Martín, N. *J. Phys. Chem*., submitted.

[37] Janssen, R. A. J.; Christiaans, M. P. T.; Hare, C.; Martín, N.; Sariciftci, N. S.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1995**, *103*, 8840.

portionwise to a solution of 150 mg (0.17 mmol) of **2** in 6 mL of dry THF. The mixture was stirred at room temperature for 90 min. and then 10 mL of water were added. The mixture was extracted twice with dichloromethane, the combined organic layers were dried over magnesium sulfate, and the solvent was removed under vacuum to yield a solid residue which was chromatographed (silica gel, hexane 1/dichloromethane 1) to afford 36 mg (18%) of **1** (*all-trans*) as a red solid: mp 41−43 °C; $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.82 (d, 2H, $J = 9.0$ Hz), 7.78 (s, 2H), 7.38 (d, 2H, $J = 8.8$ Hz), 7.31 (d, 2H, $J = 8.8$ Hz), 7.09 (d, 2H, $J = 8.8$ Hz), 6.88 (d, 2H, $J_{\mathrm{trans}} = 15.9$ Hz), 6.53 (d, 2H, $J_{\mathrm{trans}} = 15.9$ Hz), 6.33 (s, 6H), 3.95−3.88 (m, 4H), 1.49 (s, 4H), 1.34−0.84 (m, 36H), 0.79 (t, 6H, $J = 6.2$ Hz); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 155.0, 136.2, 133.9, 132.3, 131.4, 129.4, 129.1, 127.2, 125.9, 123.3, 120.4, 119.5, 118.9, 117.6, 115.9, 112.2, 108.7, 69.5, 32.0, 29.7, 29.5, 29.4, 29.3, 29.1, 25.7, 22.7, 14.1; FTIR (KBr, cm$^{-1}$) 3018, 2926, 2852, 1624, 1215. Anal. Calcd for $C_{60}H_{70}O_2S_8$: C, 66.74; H, 6.53; S, 23.10. Found: C, 65.85; H, 6.71; S, 21.90.

**Method 2.** Under argon atmosphere, 0.15 mL of a 1.0 M solution of lithium ethoxide in ethanol were added dropwise to a solution of 100 mg (0.075 mmol) of **1** and 34 mg (0.15 mmol) of formyltetrathiafulvalene (**12a**)[23] in 20 mL of absolute ethanol. After 90 min the reaction was allowed to cool at room temperature and the solvent was removed under vacuum. The solid residue obtained was chromatographed (silica gel, hexane 1/dichloromethane 1) to yield 56 mg (69%) of **1** (mixture of isomers) as a red solid.

The spectral data recorded for this mixture are similar to that obtained by using method 1 but with a higher degree of complexity due to the presence of mixture of isomers.

**(*R*)-6,6′-Bis[4″(tetrathiafulvalenyl)butadienyl]-2,2′-didodecyloxy-1,1′-binaphthalene (6).** By using the reaction conditions described in method 1 and using bisphosphonate **2** and the vinylogous formyltetrathiafulvalene **12b**[24] as starting materials, tetrathiafulvalene dimer **6** (*all-trans*) was obtained as a red solid in a 18% yield: mp 73−75 °C; $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.81 (d, 2H, $J = 9.0$ Hz), 7.68 (s, 2H), 7.30 (d, 2H, $J = 9.0$ Hz), 7.31−7.30 (m, 2H), 7.01 (d, 2H, $J = 8.9$ Hz), 6.80−6.69 (m, 6H), 6.41 (d, 4H, $J_{\mathrm{trans}} = 16.0$ Hz), 6.28 (d, 4H, $J_{\mathrm{trans}} = 16.0$ Hz), 3.90−3.81 (m, 4H), 1.35−0.84 (m, 40H), 0.79 (t, 6H, $J = 6.3$ Hz); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 155.1, 136.1, 134.7, 133.9, 132.9, 132.1, 129.3, 129.2, 127.2, 127.0, 125.9, 123.5, 123.2, 123.1, 120.5, 119.0, 117.5, 115.9, 69.8, 32.1, 29.9, 29.7, 29.6, 29.5, 29.3, 25.8, 22.9, 14.3; FTIR (KBr, cm$^{-1}$) 2922, 2850, 1560, 1458, 1248, 974. Anal. Calcd for $C_{64}H_{74}O_2S_8$: C, 67.92; H, 6.59; S, 22.66. Found: C, 67.57; H, 6.83; S, 21.45.

**Synthesis of TCAQ Dimers. (*R*)-6,6′-Bis[2″(11,11,12,12-tetracyanoanthraquinodimethan-2-yl)vinyl]-2,2′-didodecyloxy-1,1′-binaphthalene (7).** Under argon atmosphere, 3 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of 80 mg (0.06 mmol) of **1** and 40 mg (0.12 mmol) of 2-formyl-11,11,12,12-tetracyano-9,10-anthraquinodimethane (**13)**[27] in 10 mL of dry dichloromethane at 0 °C. Two minutes later, the crude reaction was poured on the top of a silica gel column where it was eluted with a hexane/ethyl acetate (7/3) mixture to yield 46 mg (60%) of **7** (*trans* isomer) as a red solid: mp 118−120 °C; $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.29 (s, 2H), 8.29−8.21 (m, 6H), 7.98 (d, 4H, $J = 8.0$ Hz), 7.82−7.71 (m, 8H), 7.47 (d, 2H, $J_{\mathrm{trans}} = 15.2$ Hz), 7.44 (d, 2H, $J = 8.8$ Hz), 7.15 (d, 2H, $J_{\mathrm{trans}} = 15.2$ Hz), 7.14 (s, 2H), 3.92 (t, 4H, $J = 6.4$ Hz), 1.32 (m, 12H), 1.18 (s, 12H), 0.93 (s, 16H), 0.77 (t, 6H, $J = 6.2$ Hz); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 160.5, 159.7, 155.6, 142.5, 135.0, 134.5, 132.5, 132.3, 130.9, 130.4, 129.8, 129.5, 129.0, 128.2, 127.8, 127.6, 126.2, 124.9, 124.6, 123.5, 115.9, 113.3, 113.2, 113.1, 83.1, 69.5, 31.9, 29.7, 29.6, 29.4, 29.2, 25.7, 22.6, 14.1; FTIR (KBr, cm$^{-1}$) 2922, 2851, 2224, 1589, 1545, 1464, 1240; EM *m*/*z* (ESI) (%I) 1302 (M$^{+}$ + 23, 100). Anal. Calcd for $C_{88}H_{78}N_8O_2$: C, 82.60; H, 6.14; N, 8.76. Found: C, 73.88; H, 6.60; N, 6.70.

**3-[2′-(11,11,12,12-Tetracyano-9,10-anthraquinodimethane)methoxicarbonyl]propionic Acid (16).** Under argon atmosphere, 240 mg (2.4 mmol) of succinic anhydride (**15**), 293 mg (2.4 mmol) of 4-(dimethylamino)pyridine, and 0.24 mL (3.0 mmol) of dry pyridine were added to a solution of 100 mg of 2-(hydroxymethyl)-11,11,12,12-tetracyano-9,10-anthraquinodimethane (**14**) in 30 mL of dry dichloromethane. The mixture was stirred at room temperature for 2 h and then was poured into an ice/water mixture. The mixture was allowed to reach room temperature, the organic layer was separated, and the aqueous layer was extracted twice with chloroform. The combined organic layers were washed with water, dried over magnesium sulfate and the solvent was finally removed under vacuum. The residue obtained was chromatographed (silica gel, ethyl acetate 8/methanol 2) to yield 125 mg (69%) of **16** as a yellow solid: mp 198−200 °C; $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.22−8.13 (m, 4H), 7.71−7.58 (m, 3H), 5.23 (s, 2H), 2.57 (s, 4H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 141.5, 132.7, 131.2, 130.8, 130.3, 130.2, 129.8, 128.0, 127.8, 127.8, 126.4, 113.1, 83.6, 83.3, 64.9, 28.8. FTIR (KBr, cm$^{-1}$) 3421, 2924, 2852, 2226, 1740, 1707, 1560, 1157; EM (EI) *m*/*z* (%I) 334 (4), 318 (100), 291 (29), 263 (23), 56 (25). Anal. Calcd for $C_{25}H_{14}N_4O_4$: C, 69.12; H, 3.25; N, 12.90. Found: C, 69.46; H, 3.41; N, 12.05.

**Dimer 8.** Under argon atmosphere, 28 mg (0.14 mmol) of 1,3-dicyclohexylcarbodiimide and 8.5 mg (0.07 mmol) of 4-(dimethylamino)pyridine were added to a suspension of 63 mg (0.14 mmol) of the TCAQ derivative **16**. After stirring the mixture at room temperature for 25 min., a solution of 45 mg (0.07 mL) of binaphthyl derivative **3** in 5 mL of chloroform were added and the reaction was stirred for additional 3 h. Then, 20 mL of water was added, and the organic layer was separated. The aqueous layer was extracted twice with chloroform, and the combined organic layers were dried over magnesium sulfate. The solvent was removed under vacuum to obtain a residue that was chromatographed (silica gel, hexane 6/ethyl acetate 4) to afford 47 mg (44%) of **8** as an orange solid: mp 96−98 °C; $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.17 (m, 8H), 7.84 (d, 2H, $J = 9.0$ Hz), 7.73 (s, 2H), 7.67−7.54 (m, 6H), 7.34 (d, 2H, $J = 9.0$ Hz), 7.03−6.92 (m, 4H), 5.16 (s, 4H), 5.13 (s, 4H), 3.85 (t, 4H, $J = 6.4$ hz), 2.66 (s, 8H), 1.66−1.55 (m, 8H), 1.35−0.92 (s, 32H), 0.81 (t, 6H, $J = 6.7$ Hz); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 172.2, 172.0, 159.7, 155.1, 141.6, 134.0, 132.6, 131.2, 130.7, 130.5, 130.3, 129.7, 129.4, 128.9, 127.9, 127.7, 126.5, 126.0, 120.4, 116.1, 113.1, 83.6, 69.7, 67.0, 64.7, 49.3, 34.1, 32.0, 29.8, 29.6, 29.5, 29.3, 29.1, 25.8, 25.0, 22.8, 14.2; FTIR (KBr, cm$^{-1}$) 2926, 2851, 2227, 1737, 1626, 1566, 1151; EM *m*/*z* (ESI) (%I) 1538 (M$^{+}$ + 23, 100), 1121 (23), 247 (21). Anal. Calcd for $C_{96}H_{90}N_8O_{10}$: C, 76.07; H, 5.98; N, 7.39. Found: C, 77.06; H, 6.45; N, 7.21.

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**Supporting Information Available:** Figures S1 and S2 shows the PM3 equilibrium geometry for a model compound of TTF dimer **5** and TCAQ dimer **8** respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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