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Enhancement of the π -electron delocalization and fluorescence efficiency of 1,6-diphenyl-1,3,5-hexatriene by covalent rigidification

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Abstract

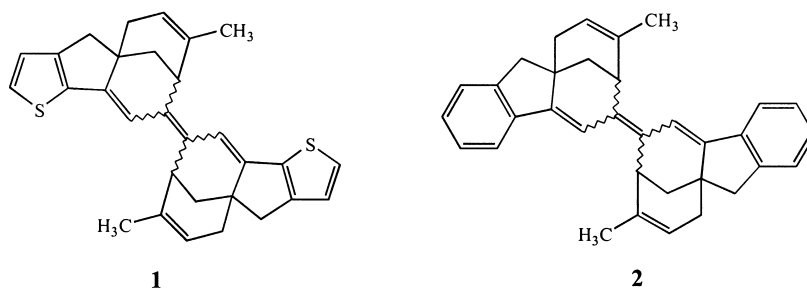
Bridged 1,6-diphenyl-1,3,5-hexatrienes were prepared from 1-indanone by successive Robinson annulation and McMurry coupling reaction. Rigidification produces a decrease in oxidation potential and HOMO-LUMO gap, and a considerable enhancement of fluorescence quantum yield compared to the open-chain analog. © 2000 Elsevier Science Ltd. All rights reserved.

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Linear π -conjugated systems (LCSs) are subject to a considerable interest related to their use as conjugating spacers in chromophores for nonlinear optics,¹ as active materials in organic field effect transistors² or in organic light emitting diodes.³ Each of these applications requires specific properties such as optimal π -delocalization, low ionization potential, high electron affinity and controlled absorption and emission spectra. Since these properties are related to the HOMO and LUMO levels and to their energy difference, the control of the HOMO-LUMO gap (ΔE) appears as a key issue for the construction of LCS specifically tailored for a given application.⁴

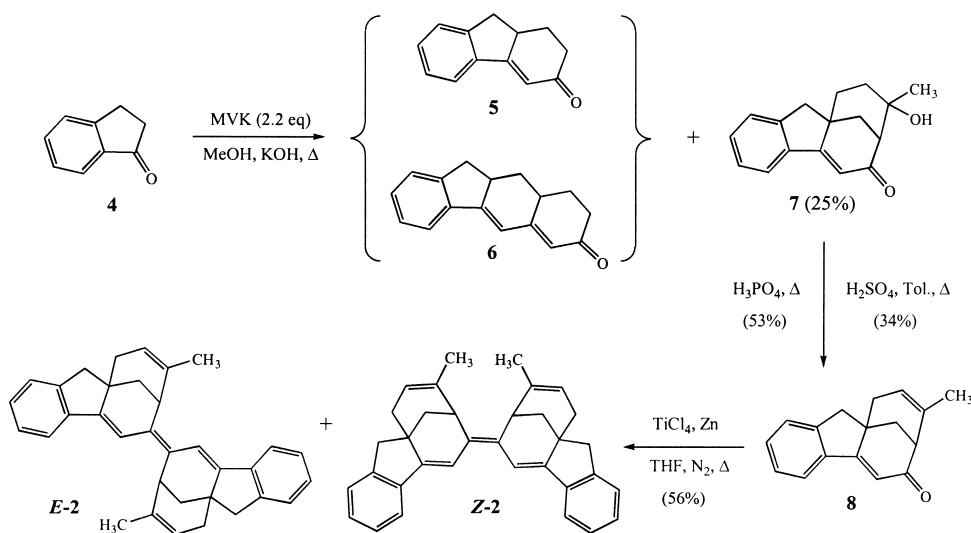
We have already shown that covalent bridging of thiophene based-LCSs allows a significant reduction of ΔE .^{5a–e} In particular, rigidification of 1,6-dithienyl-1,3,5-hexatriene **1**, produces an enhancement of the π -delocalization accompanied by a considerable increase of the photoluminescence quantum yield and thermal stability (Scheme 1).^{5f,g} As a further step we report here an extension of this approach to the case of the benzenic analog of **1** namely 1,6-diphenyl-1,3,5-hexatriene **2**.

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Scheme 1.

A Robinson annulation⁶ reaction using commercially available 1-indanone **4** and methylvinyl ketone (MVK) in the presence of KOH as base in refluxing anhydrous MeOH for 18 h led to a mixture of several products (Scheme 2). Column chromatography on silica gel (eluent:CH₂Cl₂/EtOAc 8:2) allowed to separate unreacted starting material **4**, and a fraction containing a mixture of inseparable compounds **5** and **6** resulting from mono and double Robinson annulations. The composition of this mixture was determined by both ¹H NMR and mass spectrometry. A third and main fraction corresponding to the alcohol **7** (25%) was recovered as a mixture of two couples of diastereomers in the 85:15 ratio as estimated by ¹H NMR. These compounds result from a double Robinson annulation^{5g} which implies a deprotonation process at the carbon in γ position to the ketone functionality of compound **5**. Further dehydration reaction to give compound **8** was carried out either in refluxing toluene for 1 h in the presence of H₂SO₄ or in 85% H₃PO₄ at 100°C for 10 h.



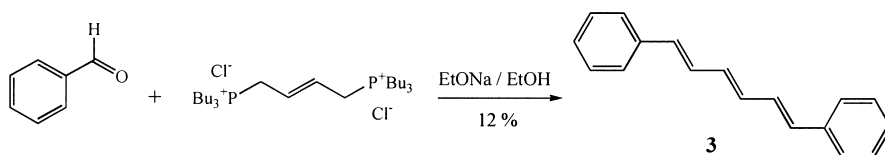
Scheme 2.

A McMurry reaction⁷ on ketone **8** using TiCl₄/Zn in refluxing anhydrous THF for 2 h gave the title compound **2** in 56% yield after column chromatography on silica gel (eluent petroleum ether/CH₂Cl₂, 9:1). The existence of two methylene bridgeheads in **2** associated with the possibility of *E* and *Z* configurations for the central carbon-carbon double bond could lead to the presence

of four separable isomers. Indeed, an additional preparative thick layer chromatography allowed the separation of two fractions F1 (20%) and F2 (30%), each of them corresponding to only one diastereomer, as confirmed by ^1H and ^{13}C NMR.⁸ The electronic absorption spectra of F1 and F2 in 95% EtOH reveals a red shift of the wavelength of the 0–0 absorption band (λ_{0-0}) from 391 to 398 nm indicative of a larger conjugation for F1 characteristic of an *E* configuration. In addition, based on previous UV–visible and X-ray data in the thiophene serie,^{5f,g} F1 and F2 can be assigned to the *E-2* and *Z-2* isomers, respectively.

In order to examine the influence of the rigidification in compounds *E-2* and *Z-2*, the reference compound **3**⁹ has been prepared by a twofold Wittig reaction between benzaldehyde and (*E*)-but-2-ene-1,4-diylbis(tributylphosphonium)dichloride (Scheme 3).¹⁰ The all-*trans* configuration of compound **3** was confirmed by the ^1H NMR spectrum in CDCl_3 which shows a proton spin-coupling constant of 15.4 Hz for the protons of the external carbon–carbon double bonds.

The optical and electrochemical data of compounds **2** and **3** are collected in Table 1. The electronic absorption spectra of *E-2*, *Z-2* and **3** show a well-resolved vibronic fine structure characteristic of a rigid structure. Furthermore, the covalent bridging in *E-2* and *Z-2* induces a red shift of λ_{0-0} of 28 and 21 nm, respectively, compared to the reference compound **3**, indicating an enhancement of π -electron delocalization.



Scheme 3.

Table 1
Optical and cyclic voltammetry data

Compd	λ_{0-2} (nm) ^a	λ_{0-1} (nm) ^a	λ_{0-0} (nm) ^a	$\lambda_{em,max}$ (nm) ^a	ϕ ^{a,b}	Epa ₁ (V) ^c	Epa ₂ (V) ^c
3	335	351	370	426	0.20	1.16 ^d	-
<i>Z-2</i>	356	374	391	434	0.29	0.89	1.18 ^d
<i>E-2</i>	356	376	398	435	0.64	0.87	1.17 ^d

^a in 95% EtOH,

^b determined at 25°C using anthracene as standard ($\phi = 0.27$ in 95% EtOH) with $\lambda_{exc} = 340$ nm,

^c 1 mM of compd in *n*-Bu₄NPF₆/CH₂Cl₂ 0.1 M, Pt working electrode, Ag/AgCl reference electrode, 0.1 V s⁻¹.

^d irreversible wave

The electrochemical behavior of *E-2*, *Z-2* and **3** was investigated by cyclic voltammetry (CV). While compound **3** shows an irreversible one electron oxidation with an anodic current peak Epa₁ at 1.16 V corresponding to the generation of the cation-radical, the CV of compounds *E-2* and *Z-2* shows a first reversible oxidation with Epa₁ = 0.87 V and 0.89 V, respectively, followed by a quasi reversible wave corresponding to the formation of the dication and peaking at 1.17 V and 1.18 V, respectively (Fig. 1). These results confirm that, as already observed for **1**,^{5f,g} rigidification of the conjugated system of **3** raises the energy level of the HOMO, which is consistent with the reduction of the ΔE indicated by optical data.

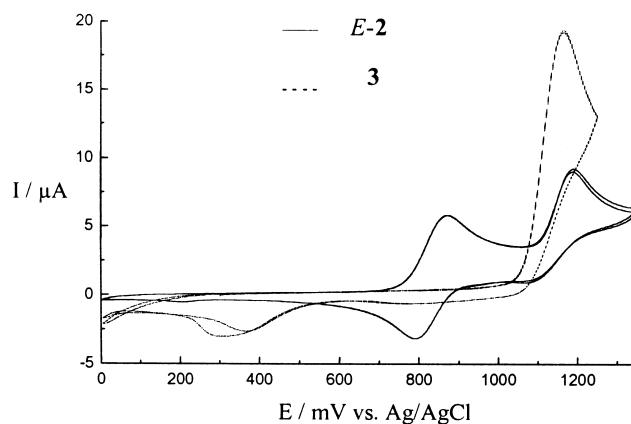


Figure 1. Cyclic voltammograms of *E-2* and **3** (see Table 1 for conditions)

The fluorescence emission spectra of *E-2*, *Z-2* and **3** correspond to the mirror image of their absorption spectra and show a well-resolved vibronic fine structure reflecting the rigid structure of the excited state. The emission maximum occurs at ca. 430 nm which corresponds to a blue light emission. Furthermore, comparison of the fluorescence intensity measured under identical conditions shows that rigidification of **3** produces a threefold increase of the emission quantum yield which reaches a value of 0.64 for *E-2* (Fig. 2).

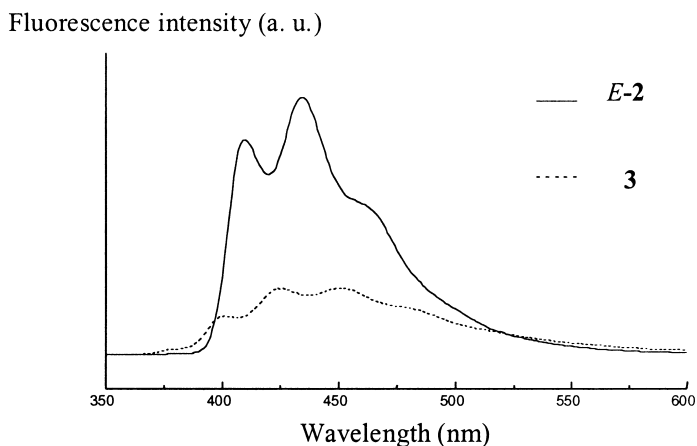


Figure 2. Relative fluorescence emission spectra of *E-2* and **3** in 95% EtOH

To summarize, the covalent bridging of 1,6-diphenyl-1,3,5-hexatriene leads to a significant decrease of the HOMO-LUMO gap due to an increase of the HOMO level, associated with a considerable enhancement of the fluorescence efficiency. Although the bridged compounds *E-2* and *Z-2* (mp > 250°C) display higher melting points than reference **3** (198–200°C), further DSC experiments should confirm the better thermal stability of bridged structures as observed in the thiophene series.^{5f,g}

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8. All new compounds gave satisfactory spectroscopic data. Compound **8**: yellow powder, mp 134–135°C, MS *m/z* (I%) EI: 236 (M⁺, 100); 221 (23); 208 (26); 192 (47); 155 (53); 127 (46); 115 (28); 89 (15); 77 (12); ¹H NMR (CDCl₃) δ : 7.51 (d, ³J = 7.6 Hz, 1H_{arom}); 7.38 (t, ³J = 7.3 Hz, 1H_{arom}); 7.33 (d, ³J = 7.3 Hz, 1H_{arom}); 7.28 (t, ³J = 7.4 Hz, 1H_{arom}); 6.16 (s, 1H_{ethyl}); 5.37 (m, 1H_{ethyl}); 3.08 (d, ²J = 15.9 Hz, 1H, CH-φ); 2.92 (d, ²J = 15.9 Hz, 1H, CH-φ); 2.89 (m, 1H, CH-C=O); 2.37 (br. d, ²J = 16.8 Hz, 1H); 2.30 (br. d, ²J = 12.3 Hz, 1H, CH₂); 2.24 (dd, ²J = 12.3 Hz, ³J = 2.8 Hz, 1H, CH₂); 2.14 (br. d, ²J = 16.8 Hz, 1H, CH₂); 1.77 (br. s, 3H, CH₃); ¹³C NMR (CDCl₃) δ : 198.8; 168.7; 146.4; 137.5; 131.9; 131.4; 127.4; 125.8; 123.4; 121.3; 115.7; 50.34; 46.0; 43.2; 37.1; 36.3; 21.8; IR (KBr) ν/cm⁻¹: 1657 (C=O). Compound **E-2**: yellow powder, mp 258°C, MS *m/z* (I%) EI: 440 (M⁺, 100); 221 (49); 179 (16); 141 (10); 129 (17); 55 (15); ¹H NMR (CDCl₃) δ : 7.45 (d, ³J = 7.6 Hz, 2H_{arom}); 7.25 (d, ³J = 7.8 Hz, 2H_{arom}); 7.19 (m, 4H_{arom}); 7.03 (s, 2H_{ethyl}); 5.23 (br. s, 2H_{ethyl}); 3.66 (br. s, 2H, CH-C=O); 2.90 (d, ²J = 15.5 Hz, 2H, CH-φ); 2.82 (d, ²J = 15.5 Hz, 2H, CH-φ); 2.20 (d, ²J = 17.4 Hz, 2H); 2.15 (dd, ²J = 11.3 Hz, ³J = 3.4 Hz, 2H); 2.08 (dd, ²J = 17.4 Hz, 2H); 1.81 (d, ²J = 11.3 Hz, 2H); 1.26 (br. s, 6H, CH₃); ¹³C NMR (CDCl₃) δ : 148.6; 144.6; 140.6; 136.5; 133.3; 127.8; 126.7; 125.4; 120.8; 119.5; 116.6; 45.9; 42.8; 38.5; 37.4; 36.1; 22.0. Compound **Z-2**: yellow powder, mp > 250°C, MS *m/z* (I%) EI: 440 (M⁺, 100); 221 (49); 179 (16); 141 (10); 129 (17); 55 (15); ¹H NMR (CDCl₃) δ : 7.50 (m, 2H_{arom}); 7.25 (m, 2H_{arom}); 7.23–7.16 (m, 4H_{arom}); 7.09 (s, 2H_{ethyl}); 5.26 (br. s, 2H_{ethyl}); 3.66 (br. s, 2H, CH-C=O); 2.93 (d, ²J = 15.5 Hz, 2H, CH-φ); 2.84 (d, ²J = 15.1 Hz, 2H, CH-φ); 2.20 (m, 4H); 2.10 (m, 2H); 1.87 (d, ²J = 11.3 Hz, 2H); 1.74 (br. s, 6H, CH₃); ¹³C NMR (CDCl₃) δ : 148.6; 144.4; 140.5; 136.0; 133.1; 127.8; 126.7; 125.3; 121.1; 120.3; 114.8; 45.9; 42.8; 39.0; 38.5; 36.2; 21.9.
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