A pyrene based dyad and triad leading to a reversible chemical and redox optical and magnetic switch


Abstract: Two new pyrene-polychlorotriphenylmethyl (PTM) dyads and triads have been synthesised and characterized by optical, magnetic and electrochemical methods. The interplay between the different electronic states of the PTM moiety in the dyads and triads and the optical and magnetic properties of the molecules have been studied. The electronic spectra of the radicals 5' and 6' show the intramolecular charge-transfer (ICT) transition at around 700 nm due to the acceptor character of the PTM radical. In the diamagnetic protonated derivatives 3 and 4 the fluorescence due to the pyrene is maintained, whereas in the radicals 5' and 6' and the corresponding anions 5 and 6 there is a clear quenching of the fluorescence, being more efficient in the case of radicals. The redox activity of PTM radicals that are easily reduced to the corresponding carbanion has been exploited to fabricate electrochemical switches with optical and magnetic response.

Introduction

The design of novel molecules able to process information such as the molecular systems involved in the living organisms is a current topic of research. Bistable molecules that can be externally interconverted between two or more states exhibiting different properties represent suitable platforms to fabricate molecular switches as a base of logic operations.[1,2] Such processes can be visualized as a transformation of inputs into outputs. Fluorescent emission and optical absorption are highly attractive output signal responses due to the fact that they are very sensitive and involve easy and low cost detection procedures.[3] Chemical inputs taking advantage for instance of host-guest interactions or acid-base reactions have been employed to trigger molecular transformations.[4] Further, optical and electrochemical stimuli have also been proved to be very efficient to reversibly interconvert photo- or electroactive molecules, respectively. In particular, in this work new dyads and triads based on pyrenyl (Pyr) and polychlorotriphenylmethyl radical (PTM) moieties have been synthesized in order to be applied as molecular switches. Pyr groups are well-known fluorescent cores, the fluorescence of which can be quenched by photo-induced electron transfer processes.[5,6] In addition, PTM derivatives show distinctive absorption characteristics and, in their radical form, their electroactive character can be used to modulate the magnetic and optical properties of the materials.[7] The PTM radicals have their open-shell centers sterically shielded by six bulky chlorine atoms which ensure their persistency and thermal and chemical stabilities.[8] Thus, we show here that the combination of these two functional moieties offers a promising approach to synthesize a novel class of switchable materials.

Results and Discussion

Synthesis of the pyrene substituted polychlorotriphenylmethyl (PTM) radicals 5' and 6' was performed following the synthetic approach depicted in Scheme 1. First, polychlorinated triphenylmethane (α-H-PTM) bis-phosphonate and bis-phosphonium bromide salt derivatives 1 and 2 were prepared from the corresponding α-H-PTM bis-bromomethyl derivative.[9] Coupling of those compounds under Wittig conditions with 1-pyrenecarboxaldehyde leads to a mixture of α-H-PTM mono and bisadducts 3 and 4 in different proportions depending on the starting compound used: bis-phosphonate 1 leads to a 1:9 proportion of 3:4, whereas with bis-phosphonium salt 2 the ratio was found to be 1:1. Treatment of 3 and 4 with an excess of tetrabutylammonium hydroxide promotes the removal of the acidic proton at the α-position to give the corresponding carbanions that were subsequently oxidized in situ using a concentrated solution of AgNO3 in MeCN to yield the target radicals 5' and 6'. Both radicals show characteristic lines in the Electronic Spin Resonance (ESR) spectra corresponding to the coupling of the free electron with the protons of the vinylene bonds (Figure S1).[10] Radical 5' ESR spectrum shows two principal broad lines showing a coupling constant of \(a_H = 1.95\) G. The coupling with the other vinylenic proton and the protons of the methyl group is small and contributes to the broadening of the lines. According to its structure, radical 6' shows a three line spectrum due to the coupling of the radical with two of the protons of the two vinylene bonds, with a coupling constant of \(a_H = 1.90\) G.
The redox properties of all compounds in solution were studied by cyclic voltammetry (CV) (Table 1). As shown in Figure 1 (grey line) the CV for compound 5• displays two reversible processes at E1/2 = -0.70 V and E1/2 = 0.68 V (vs. Fc+/Fc). The cathodic process corresponds to the reduction of the PTM radical sub-unit to the corresponding anion[7,11] while the anodic peak is attributed to the oxidation of the pyrenyl sub-unit. In the corresponding oH compound 3 the oxidation of the pyrenyl subunit is observed as a less reversible peak and at higher potential, E1/2 = 0.88 V (vs. Fc+/Fc) (Figure SI2). CV of compound 6• (Figure 1 black line) shows the reduction wave at E1/2 = -0.72 V (vs. Fc+/Fc), and two oxidation processes at E1/2 = 0.64 V and E1/2 = 0.85 V attributed to the stepwise oxidation of the two pyrenyl sub-units.

Table 1. Redox Potentials of Compounds 3-6 and radical PTM-CH3[a] in V vs Fc+/Fc in CH2Cl2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E1/2 red</th>
<th>E1/2 ox1</th>
<th>E1/2 ox2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5•</td>
<td>-0.70</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>6•</td>
<td>-0.72</td>
<td>0.64</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>0.88</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>0.78</td>
</tr>
<tr>
<td>PTM-Me</td>
<td>-0.58</td>
<td></td>
<td>1.19</td>
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[a] ref. 12 [b] quasi reversible wave.

The observation of two redox processes for the pyrenyl subunits of 6 indicate a strong electronic interaction of the pyrenyls through the PTM radical bridge. To rationalize if the big splitting of the redox processes can be due to the formation of an intermediate species with a very strong spin-spin interaction when the cation radical of pyrene is formed, we have studied the ESR spectra of the one electron oxidized species of radicals 5• and 6• generated “in situ”. In both cases silent ESR spectra were obtained. In other words, the ESR signal corresponding to the PTM radical disappears and no new signals due to the pyrene cation radical appears, meaning that the formed biradicals are in the singlet ground state possibly forming the closed-shell species depicted in scheme 2. The formation of these species can also explain the lowering of the first oxidation potential in radicals 5• and 6• with respect to their oH counterparts 3 and 4 as well as the high reversibility of these processes, since it is known that the oxidation of Pyr units tend to result in not so reversible CV waves as in the case of 3 and 4.

Scheme 2. Possible closed-shell forms derived of the 1 e oxidations of radicals 5• and 6•.
Figure 2. a) UV-Vis spectra of αH-PTM 3 (green line), anion 5⁻ (blue line) and radical 5• (red line). Insets: photographs of the cuvettes containing 7x10⁻⁵M solutions of 3, 5⁻ and 5• in THF and low energy region spectrum of a more concentrated solution of radical 5• showing the ICT band. b) Fluorescence spectra of αH-PTM 3 (green line), anion 5⁻ (blue line) and radical 5• (red line). Inset: photographs of cuvettes under 366 nm light containing 2.5x10⁻⁵M solutions of 3, 5⁻ and 5• in THF.

The UV-visible spectrum of 3 in THF shows a broad absorption band in the visible range with an absorption maximum centered at 370 nm, assignable to the pyrenyl chromophore, and that is in accordance with the pale green color of the solution (Figure 2a, Table S11). Radical 5• solution has a brown color and accordingly displays in the visible region, four more bands: an intense band at 380 nm, two broad and weak bands at 518 nm and 601 nm that are characteristic of the PTM radical. The carbanion solution shows an intense violet color and three bands in the visible region of the spectrum, the one corresponding to the pyrenyl moiety at 365 nm, and two broad and intense bands at 518 nm and 601 nm that are characteristic of the PTM anion chromophore. Similar spectral features are found in the analogous bis-substituted derivatives 4, 6• and 6⁻, the only difference arising from the relative intensities of the bands corresponding to the pyrenyl and PTM moieties (Figure S13 and table S11). Thus, it is clear that the three forms of the PTM derivatives (αH, radical and anion) give distinct absorption properties.

The fluorescence characteristics of the synthesized materials were also explored since it is well known that pyrene groups give a strong fluorescence (Table S1). In agreement to this, the protonated derivative 3 shows an intense fluorescence. The emission spectrum in THF (Figure 2b) displays typical excimer emission band at 484 nm (λexc = 380 nm) with high quantum yield (Φ = 0.0147), which is similar to those exhibited by pyrene derivatives in which the fluorescence emission is not quenched. However, the emission spectra of radical 5• and the corresponding reduced species 5⁻ in THF are completely different (Figure 2b). The fluorescence intensity decreases one order of magnitude, and displays the typical monomer emission bands at 423, 444, 486 and 517 nm (λexc = 380 nm) with well-resolved vibronic features, and low quantum yield (Φ = 0.0018 for 5⁻ and Φ = 0.0009 for 5•). Both such spectra are similar to that of pyrene derivatives in which the fluorescence emission is quenched. The difference between anion and radical spectra is only the intensity of the emission bands, the anion showing higher intensity than the radical, which implies that the pyrene fluorescence quenching is more effective with the radical moiety than with the anionic one. The same results were obtained with the bi-substituted derivatives 4, 6• and 6⁻ (Figure S14 and Table S11).

The observed fluorescence emission quenching in PTM-Pyrene hybrids can occur via electron-transfer following one of the two quenching pathways shown in Figure 3, similar to those previously described for the fluorescence quenching of phthalocyanine and anthracene by other electroactive molecules like tetraethylfulvalenes. In accordance with their electronic characteristics, PTM radical 5• is a quite good electron acceptor, whereas PTM anion species 5⁻ is a very good electron donor. Therefore, electron transfer can occur easily from the HOMO of the anionic ground state to the HOMO of the excited pyrene (Pyr*) that due to photoexcitation increases its acceptor strength, hence resulting in emission quenching. On the other hand, the photoexcitation of pyrene also results in an increase in its electron donor character, and hence, electron deficient PTM...
radical can accept electrons from Pyr*. Such electron transfer also results in emission quenching.

Figure 3. Molecular Orbital scheme of pyrene emission and emission quenching pathways.

Figure 4. Calculated (COSMO-THF/B3LYP-D3/def2-TZVPP// COSMO-THF/ B3LYP-D3/def2-TZVP) energy diagram (eV) for FMOs in αH (3), anionic (5−) and radical (5•) species. In the latter case, the α and β spin series are shown. The occupied FMOs are labelled in blue and virtual ones in red. For the most relevant FMOs, the corresponding Kohn-Sham isosurfaces (isovalue 0.04 au) are also displayed. For the sake of comparison the energy levels of 1-vinylpyrene (VPyr) are included Caption.

The above described quenching mechanisms agree with the calculated Frontier Molecular Orbitals (FMOs) in the ground state (Figure 4). For the αH-PTM compound 3, the HOMO and LUMO levels are very similar to that of the isolated pyrene, in line with the fact that the fluorescence emission in 3 is similar to that of pyrene. However, the HOMO of the anionic species 5− and the β-LUMO of the radical 5•, both centered in the PTM moiety (Figures S19-11), lie in the middle of the HOMO-LUMO gap of pyrene. This is also in accordance with the fact that these orbitals can mediate the quenching mechanism through photoinduced electron transfer processes.

As the oxidation/reduction between radical-anion PTM pair can be reversible carried out in radicals 5• and 6•, the possibility of fabricating a redox absorbance or fluorescence switch based on them aroused. To elucidate this, spectroelectrochemical studies in UV-Vis absorption and fluorescence emission were performed. Applying a voltage potential step of -0.7 V (vs Ag/AgCl) during 15 min. to a THF solution of radical 5• or 6•, led to a reduction of radicals 5• and 6• into their corresponding anions 5− and 6−, respectively. As expected, the change to the anion spectrum in absorbance (Figure 5 and S16 left) and enhancement of the fluorescence emission (Figure S15 and S16 right) was observed. A subsequent application of an oxidation potential of +0.5 V during 15 min. resulted in to the recovery of the radical absorbance spectrum and a decrease in the fluorescence intensity. After the electrochemical oxidation was completed, the initial parameters of absorbance and fluorescence of the radicals 5• and 6• solutions were completely recovered. Reduction and subsequent oxidation were carried out for several cycles. (Figures 5, S15 and S17). The absorbance spectrum and fluorescence intensity were recovered after each step demonstrating the high reversibility of the switching process and the high stability of the involved species.

Figure 5. Changes in the UV-Vis spectra of radical 5 (c = 3.6*10−5 M in THF using c = 0.05 M of Bu4NPF6) upon a chronoamperometric reduction experiment and subsequent oxidation step (15 minutes each step to reach the complete transformation). Inset: evolution of the UV-Vis intensity at 518 nm during the stepwise reduction an oxidation cycles.
Such redox transformations can also be followed by ESR since the paramagnetic radical species exhibit an ESR signal, while the anionic forms are ESR silent due to their diamagnetic character. Therefore, the magnetic output is also a useful tool to follow the switching behavior.

**Conclusions**

The synthesis of new pyrene-PTM dyads and triads has been accomplished successfully which permitted to study the interplay between the different electronic states of the polychlorotriphenylmethyl moiety and the optical and magnetic properties of the molecules. In the diamagnetic protonated derivatives 3 and 4 the fluorescence due to the pyrene is the same as in other pyrene substituted derivatives, whereas in the radicals 5 and 6 and the corresponding anions 5’ and 6’ there is a clear quenching of the fluorescence, being more efficient in the case of radicals. The fact that the PTM centered HOMO of the anionic species and the j-LUMO of the radicals lie on the middle of the HOMO-LUMO gap of pyrene is in accordance with the mediation of those orbitals in the quenching mechanism. By simple acid/base or redox reactions the compounds mimic the "AND" Boolean logic operations. Further, the redox activity of PTM radicals has been exploited to fabricate electrochemical switches with optical (i.e. absorption and fluorescence) and magnetic response.

**Experimental Section**

**General:** Elemental analyses were performed on the CDS (CSIC) services. NMR spectra were recorded on a Bruker Avance 400 MHz and 360 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (J) are given in hertz (Hz) and are quoted to the nearest 0.5 Hz. ESR spectra were recorded in a Bruker ELEXYS E500 X-band spectrometer. Electrochemical experiments were performed with a platinum wire as working and counter electrode and Ag wire as potensio/galvanostat 263 from EG&G Princeton Applied Research, by using a platinum wire as working and counter electrode and Ag wire as potensio/galvanostat 263 from EG&G Princeton Applied Research. FT-IR spectra were recorded in a Bruker ELEXYS E500 X-band spectrometers. Chemical shifts are reported in parts per million (ppm).

**Synthesis of bis(bromotriphenylphosphine)-((( perchlorophenyl)methylene)bis(2,3,5,6-tetrachloro-4,1-phenylene))bis(methylene)) salt (2).** Triphenylphosphine (5.40 g, 20.60 mmol) was added to a solution of H-PTM dibromomethyl derivative (1.50g, 1.71 mmol) in dry benzene (150 mL) and was heated under reflux for 20 h. The formed precipitate was filtered, washed with benzene, and dried under vacuum to yield pure compound 2 (2.17 g, 90.1%). 1H-RMN (400MHz, CDCl3) δ (ppm) 7.82-7.77 (m, 20 Hα), 7.68-7.76 (m, 10 Hβ), 6.83 (s, 1 Hα) 6.10-5.80 (m, 2 H), 5.64 (dd, J = 25.7 Hz, J = 15.3 Hz 2H); 13C-RMN (100.6MHz, CDCl3) δ (ppm) 138.22, 138.04, 137.99, 135.83, 135.51, 135.23, 135.11, 134.94, 134.87, 134.80, 134.33, 134.07, 132.13, 132.03, 131.93, 130.41, 130.29, 128.54, 128.43, 118.06, 117.20, 56.63 (H), 32.07(CH2), 32.57(CH3); IR (KBr): ν=1585, 1480, 1435, 1370, 1295, 1110, 955, 840, 755, 685, 495 cm^{-1}; UV/Vis (THF): λ(αm) (ε) (cm^{-1}): 305 (1630), 295 (1606), 275 (1000), 260 (904) nm; elemental analysis calculated (%): for C36H26BrCl2P: C 48.81, H 2.52, Br 11.38, Cl 31.84.

**Synthesis of bis((1E,1’E)-((( perchlorophenyl)methylene)bis(2,3,5,6-tetrachloro-4,1-phenylene))bis(ethene-2,1-diyl))dipyrine (4) and (E)-2,3,5,6-tetrachloro-4-(( perchlorophenyl)bis(2,3,5,6-tetrachloro-4,1-phenylene))bis(methylene)methylstyrpyrene (3).** Method A: To a stirred solution of potassium tert-butoxide (47mg; 0.42mmol) in dry THF (15ml) under argon and cooled to -78°C, bis-triphenyl phosphonium salt 2 (200 mg; 0.14mmol) was added. The yellow-orange ylide solution formed was stirred for 10 min, and then the temperature was increased to 0°C with an ice bath, then 1-pyrenecarboxaldehyde (71.4mg; 0.31mmol) dissolved in 5 ml of dry THF was added. The resulting mixture was allowed to reach room temperature, and stirred for 48h, the yellow crude product was washed with water and extracted with CHCl3, and the organic layer was dried over MgSO4, filtered, and the solvent evaporated under reduced pressure. Flash chromatographic purification with silica gel (hexane/CH2Cl2 85/15) yielded compounds 3 (55mg 43%) and 4 (84 mg 41%) as a yellow powders. Compound 3: Melting point: 264-266 °C; 1H-RMN (400MHz, CDCl3) δ (ppm): 8.42 (d, J=9, H, 1Hα), 8.36 (d, J = 8.1 Hz, H, 1Hβ), 8.27 – 8.17 (m, 3Hα+1Hβ), 8.15 (d, J = 9.3 Hz, H, 1Hα), 8.12 – 8.07 (m, 2Hα), 8.03 (t, J = 7.6 Hz, 1Har), 7.28 (d, J = 16.5 Hz, 1Hα+2Hβ), 7.09 (s, 1Hα), 2.65 (s, 3H3oc); 13C-RMN (100.6MHz, CDCl3) δ (ppm): 136.03, 122.80, 127.90, 127.42, 126.17, 125.94, 125.40, 125.19, 123.95, 122.97. 56.70(OT), 29.71(CH3); UV/Vis (THF): λ(αm) (ε) (cm^{-1}) (17800), 370 (22900); Fluorescence (THF): λ(αm) (ε) (cm^{-1}) (380nm) (ε) = 484 (0.147); MALDI-TOF (negative mode) (C26H19Cl5P, M=932.4); m/z [M] = 932.1; [M-35] = 897.1. Compound 4: Melting point: 336- 337 °C; 1H-RMN (400 MHz, CDCl3) δ (ppm): 8.44 (d, J=9.3 Hz, 2H), 8.38 (d, J = 8.0 Hz, 2Hα), 8.29 – 8.19 (m, 8Hα+2Hβ), 8.16 (d, J = 9.3 Hz, 2Hα), 8.13 – 8.07 (m, 4Hα), 8.03 (t, J = 7.6 Hz, 2Hα), 7.31 (d, J = 16.4 Hz, 2Hα+2Hβ), 7.16 (s, 1Hα); 13C-RMN (100.6MHz, CDCl3) δ (ppm): 137.71, 137.11, 136.16, 136.18, 134.39, 133.51, 132.97, 132.10, 130.70, 129.01, 128.23, 127.92, 126.18, 125.99, 125.66, 125.42, 125.20, 125.04, 124.85, 123.99, 123.00, 56.95 (H); UV/Vis (THF): λ(αm) (ε) (cm^{-1}) (285 (24700), 370 (32200)); Fluorescence (THF): λ(αm) (ε) (cm^{-1}) (3800nm) (ε) = 484 (0.0260); MALDI-TOF (negative mode) (C26H19Cl5P, M=1144.6); m/z [M] = 1144.1, [M-72] = 1072.0, [M-108] = 1036.0. Method B. The same procedure as in method A, but using Bis(diethylphosphonate) derivative 1 (300mg, 0.31mmol), yielded solution compound 3 (34ng, 9%) and 4 (265mg, 75%).

**Synthesis of radical (E)-2,3,5,6-tetrachloro-4-(( perchlorophenyl)methylene)methylstyrpyrene (5).** To a solution of compound 3 (50mg, 0.05mmol) in THF (15ml), an excess (0.1 ml, 0.22 mmol) of tetrabutylammonium hydroxide (40%) in water was added. The resulting yellow mixture was stirred for 15min and then AgNO3 (56 mg, 0.33 mmol) was added and the mixture stirred for 10 min. The solution changed the colour to dark brown while silver (Ag0) precipitated. Then, the solution was filtered off to eliminate the silver and evaporated under reduced pressure. The obtained compound was filtered through silica gel with CH2Cl2 and a dark brown powder was obtained (43mg, 92%). Melting Point: 261-263 °C; ESR (CH2Cl2): g = 2.0035, JH =...
Synthesis of radical 2,2'-(1E,1'E)-([perchlorophenyl)methylene] bis[2,3,5,6-tetrachloro-4,1-phenylene] bis[ethene-2,1-diy] dipyrine (6). The same procedure as before was used for the conversion of compound 4 in the corresponding radical 6 that was obtained as a dark brown powder, yield 92%. Melting Point: 320 ºC dec.; ESR (CH 2Cl2): g= 2.0023, 1H rm = 1.10G, aH = 1.90G, aDCH2 = 9.5G, 12.5G, aDC = 29.6 G ATR-IR: 3978, 3652, 1614.4, 1509.3, 1336.8, 1319.2, 1264.5, 955.5, 838.5, 818.6, 716.1; UV/Vis (THF): ε(λ) = 285 (18800), 370 (28000), 397 (26600), 536 (4700), 587 (4000), 687 (629); MALDI-TOF (negative mode) (C83H62Cl6, M=1143.6); m/z [M] = 1144.0, [M-72] = 1072.0, [M-838.5] = 986.0, [M-818.6] = 918.5, [M-716.1] = 838.5, 818.6, 716.1; MALDI-TOF (positive mode) (C55H22Cl13, M=1143.6); m/z [M] = 1144.0, [M-72] = 1072.0, [M-1058] = 1036.0.

Computational Details: Quantum chemical calculations were performed with the ORCA electronic structure package program. All geometry optimizations were run with tight convergence criteria using the B3LYP[19] functional together with the RJCOSX algorithm[20] and the Ahlrichs’ segmented def2-TZVP basis set[21] starting from pre-optimized geometries obtained with the smaller def2-SVP basis set. [22] In all segmented def2-TZVP basis set, starting from pre-optimized functional together with the RIJCOSX algorithm [20] and the Ahlrichs’ def2-TZVPP basis set. [21] Reporteds reported energies were uncorrected for the zero-point vibrational term. Solvent effects were taken into account by using the COSMO solvation model.[22] MO diagrams (in Figures 6 of the main text and Figures SI 7, SI 8 and SI 9) were drawn with VMD.[22]

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Keywords: D-A dyads • free radical • pyrene • molecular switch • electronic states


The synthesis of new pyrene-polychlorotriphenylmethyl (PTM) dyads and triads has permitted to study the interplay between the different electronic states of the PTM moiety and the optical and magnetic properties of the molecules as well as their switching properties.

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A pyrene based dyad and triad leading to a reversible chemical and redox optical and magnetic switch