Transistors from a conjugated macrocycle molecule: field and photo effects†

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This study explores a conjugated macrocycle molecule and details its synthesis, molecular structure, assemblies in the solid state and application in phototransistors.

Arylene ethynylene macrocycles[1] are useful building blocks for porous molecular crystals,[2] carbon nanostructures,[3] fluorescent sensors,[4] polymeric nanotubes[5] and 3D molecular architectures.[6] Although such class of macrocycles has aroused a broad range of interests, exploring their use in organic electronics has not been reported. As shown in Fig. 1, **1a** has two anthracene subunits, which are useful building blocks of environmentally stable organic semiconductors for application in organic field effect transistors (OFETs),[7] linked by two diacetylene groups in a macrocycle structure. Our findings are that the thin films of macrocycle **1a** function as transistors showing not only a field effect but also a photo effect. The electrical response to photoirradiation allows the device to work as a phototransistor combining dual functions of light detection and signal magnification in a single device.[8,9] Although **1a** was first synthesized about half a century ago,[10] it was almost forgotten by chemists thereafter and this study appears to be the first for its soluble derivatives, assembly and electrical properties being investigated.

Unsubstituted macrocycle **1a** is an orange crystalline solid, which is practically insoluble in common organic solvents at room temperature and can only be dissolved in hot high-boiling-point aromatic solvents, such as 1,2,4-trichlorobenzene. To increase the solubility of **1a**, two flexible alkyl chains are introduced to the anthracene subunits. Scheme 1 shows the synthesis of macrocycles **1a** and **1b**, in which the acyclic precursors **2a,b** were prepared by modifying the reported processes.[11] The relatively good yields of **1a,b** from oxidative cyclic dimerization of **2a,b** should be related to the favorable orientation of ethynyl groups in the rigid backbones of **2a,b**.[10] **1b** dissolves in organic solvents such as chloroform and toluene at room temperature with solubility lower than 1 mg ml^{-1} and forms yellow solutions with intense green fluorescence. The ^{1}H NMR spectra of **1b** show the protons inside the macrocycle (H^a of **1b** shown in Scheme 1) having a chemical shift of 9.30 ppm, which shifts downfield compared to that of H^b (9.16 ppm) in **2b**. This is similar to the properties of kekulene[12] and indicates that the 18-membered ring of **1b** is not annulenoid-aromatic. The longest wavelength absorbance for **1a** (468 nm, obtained from a dilute solution of **1a** in 1,2,4-trichlorobenzene) is essentially the same as that of di-9-anthryldiacetylene (470 nm)[13] suggesting that the anthrylene diacetylene macrocycle has an electronic structure similar to its acyclic analogue.

To test the stability of these macrocycle molecules, **1a** and **1b** were subject to photoirradiation and heating in ambient air. Crystalline powders of **1a** and **1b** appeared stable to photoirradiation with a 500 W tungsten lamp for 12 hours. As monitored by differential scanning calorimetry (DSC), **1a** and **1b** undergo an irreversible exothermic reaction at *ca.* 402 and 320 °C, respectively prior to melting yielding insoluble black solids with a metallic luster. Micrographs of the thermal product of **2b** and DSC thermograms of **1a** and **1b** are shown in Fig. S1 of ESI.† Such exothermic reaction can be attributed to thermal polymerization of macrocycle molecules, which was reported for other arylene ethynylene macrocycles with similar structures.[14]

Slowly cooling a hot solution of **1b** in 1,2,4-trichlorobenzene resulted in orange crystals. X-Ray crystallography‡ for these crystals indicates that the macrocycle backbone is essentially flat and reveals an offset stacked orientation of the macrocycles

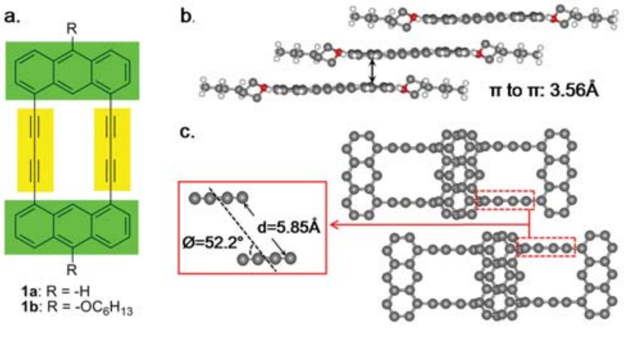

Fig. 1 (a) Molecular structure of the macrocycles with anthracene and diacetylene moieties highlighted, respectively; (b) side view of molecular packing of **1b** from the crystal structure showing the distance between π-surfaces (α-carbon atoms of hexyl groups are disordered in the crystal structure); (c) top view of offset stacked macrocycles of **1b** from the crystal structure highlighting the distance between diacetylene subunits of neighboring molecules with alkoxyl groups and hydrogen atoms omitted for clarity.

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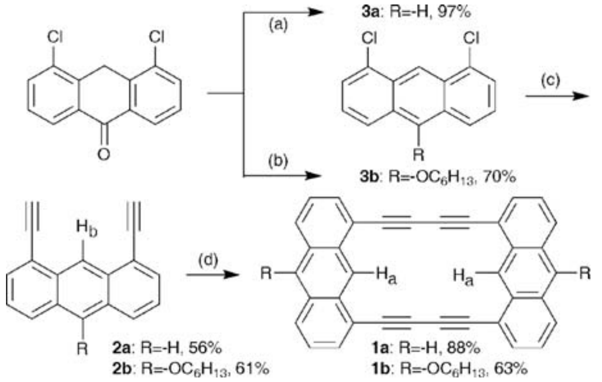

Scheme 1 Synthesis of macrocycles: (a) $NaBH_4$, *i*-PrOH, then HCl, (b) K_2CO_3, $C_6H_{13}Br$, DMF; (c) (i) trimethylsilylacetylene, CH_3MgBr, $Ni(acac)_2$, PPh_3, THF; (ii) KOH aq., THF; (d) $Cu(OAc)_2$, pyridine–CH_3OH.

as shown in Fig. 1(b) and (c). The α-carbon atoms of the hexyl groups are disordered in the crystal structure, and the hydrogen atoms on α- and β-carbon atoms are not included due to such disorder. The molecules of **1b** stack in one direction with overlap between anthracene subunits of neighboring macrocycles and a distance of 3.56 Å between aromatic planes of neighboring macrocycles. Such molecular packing should allow charge transport along the direction of π-stacking. The closet contacts between diacetylene subunits of two macrocycles are observed between neighboring stacks rather than in one stack. As shown in Fig. 1(c), the two diacetylene subunits in neighboring stacks are placed in a parallel arrangement with a distance *d* between the diyne centers of 5.85 Å and a declination angle $\varnothing$ of 52.2° between the molecular and stacking axes. It is well established that diacetylenes undergo topochemical photopolymerization to form *trans*-polybutadiyne when diacetylene monomers are arranged in tilted stacks in crystals with *d* of 4.7–5.2 Å, and $\varnothing$ of *ca.* 45°.[15] Thus the observed stability of macrocycle molecules to photoirradiation can be attributed to the molecular packing because the diyne-diyne separation (*d*) between diacetylene subunits of **1b** is too large to allow this type of topochemical photopolymerization.

Thin films of **1a** were deposited on oxidized silicon substrates by thermal evaporation in vacuum. X-Ray diffraction from the film (shown in Fig. S2 of ESI†) shows a primary diffraction peak at $2\theta = 8.80°$ (*d*-spacing: 10.04 Å) with a second-order peak at $2\theta = 17.75°$ (*d*-spacing: 5.02 Å) indicating a polycrystalline film. The relatively weak diffractions suggest low long-range orders of molecules in the thin film. The π–π interaction between molecules of **1a** was revealed by comparing the absorption spectra from a dilute solution of **1a** in 1,2,4-trichlorobenzene (3×10^{-5} M) and from a thermal evaporated film of 150 nm thick on glass (shown in Fig. S2 in ESI†). The longest wavelength absorption for **1a** shifts to the red by *ca.* 25 nm on going from solution (468 nm) to the thin film (493 nm). This type of red shift can be attributed to the delocalization of the excited state due to π-stacking and is common in many π-stacked systems.[16] Deposition of **1b** by thermal evaporation was not successful due to polymerization of **1b** prior to sublimation. On the other hand, casting a solution of **1b** on an oxidized silicon substrate yielded isolated crystals rather than continuous films possibly because of the relatively low solubility of **1b** at room temperature.

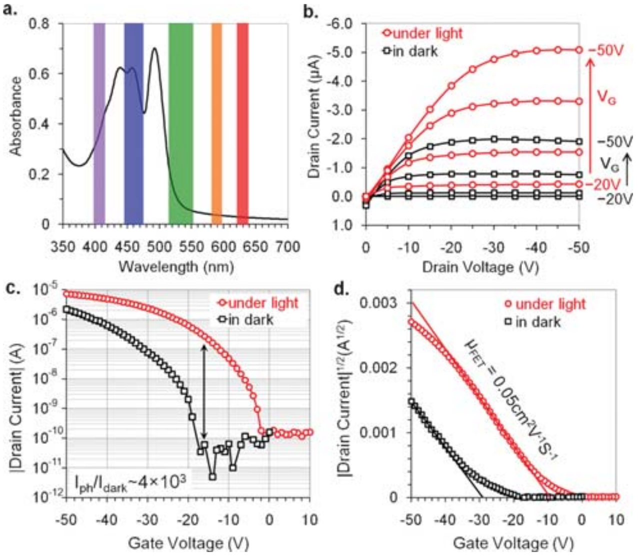

Fig. 2 (a) Absorption spectrum of **1a** in a film of 150 nm thick overlapped with color bars, which show the wavelength and half-peak width of the illumination tested in the study of phototransistors. (b) Drain current *vs.* drain voltage for the thin film transistor of **1a** deposited on OTS-treated SiO_2 at a substrate temperature of 110 °C with channel dimension of $W = 2$ mm and $L = 100$ μm tested in dark and under violet light ($\lambda = 408$ nm) of 1.0 mW cm^{-2}, respectively. (c and d) Drain current *vs.* gate voltage for the above device tested at a drain voltage of −50 V in the dark and under violet light ($\lambda = 408$ nm) of 3.9 mW cm^{-2}, respectively.

Thin-film transistors of **1a** in a top-contact configuration were fabricated by thermal evaporation in vacuum using gold as source and drain electrodes, highly n-doped silicon as a gate electrode and a 300 nm thick layer of SiO_2 as dielectric. The thin film of **1a** performs as a p-channel field effect transistor with its field effect mobility dependent on the surface treatment with a self-assembled monolayer of octadecyl trichlorosilane (OTS) and the substrate temperature during deposition. Deposition of **1a** on OTS-treated SiO_2 at a substrate temperature of *ca.* 110 °C was found to yield the best device performance with field effect mobility of 0.02–0.07 $cm^2\ V^{-1}\ s^{-1}$ in our studies. Fig. 2(b)–(d) shows typical *I–V* curves for such devices, from which a field-effect mobility of 0.05 $cm^2\ V^{-1}\ s^{-1}$ is measured in the saturation regime using the equation: $I_{DS} = (\mu W C_i/2L)(V_G - V_T)^2$ and C_i of 11 nF cm^{-2} for 300 nm SiO_2.[17,18] The on/off ratio of the drain current obtained between 0 and −50 V gate bias from the output *I–V* curves is $>1 \times 10^4$.

Interestingly thin film transistors of **1a** also show a photo effect, which was first noticed when the *I–V* characteristics were measured under white light from a halogen lamp. To test the photo effect, five LED lamps were used as sources of visible light with varied colors, which are shown in Fig. 2(a) with the absorption spectrum of **1a** in a thin film. It is found that irradiation with violet, blue and green light, which have photon energy higher than the HOMO–LUMO gap of **1a** in the solid state (about 550 nm as estimated from the edge of longest wavelength absorption), causes the threshold voltage to shift without apparently changing the charge carrier mobility. Such effect indicates that light functions as an additional parameter to control the number of mobile charges. As shown in Fig. 2(d), upon irradiation with violet light (λ = 408 nm) of 3.9 mW cm^{-2} the threshold voltage shifts from −29 V to −9 V. A ratio of photo-current and dark-current ($I_{\text{ph}}/I_{\text{dark}}$) as high as 4×10^3 is measured from the transfer curves shown in Fig. 2(c). In contrast, transistors of **1a** do not show response to orange and red light. Such photo effect can be attributed to charges generated by dissociation of photo-induced excitons.[8,9] The relatively large threshold voltage (−29 V) suggests high density of charge carrier traps in the transistor.[17] Photo irradiation shifts the threshold voltage to less negative values because some of the traps are filled with the photo-induced charges.

In summary, the studies above demonstrate that the thin films of macrocycle **1a** function as phototransistors combining light detection and signal magnification in a single device. The photo response suggests potential applications of this family of conjugated macrocycle molecules in organic optoelectronics, such as photodetectors and solar cells. The success of using conjugated macrocycle molecules as organic semiconductors in OFETs[19] also suggests a new strategy to design electronic materials for OFET-based chemical sensors since the intrinsic cavity from a macrocyclic structure may selectively bind a guest molecule. For such application, the cavity inside the conjugated macrocycle should be enlarged to accommodate a guest molecule. Investigations on conjugated macrocycles with larger cavities are in progress in our laboratory.

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Notes and references

‡ *Crystal data* for **1b**: $C_{48}H_{40}O_2$: M = 648.80, triclinic, space group $P\bar{1}$, a = 8.9279(8), b = 10.0248(9), c = 11.7180(10) Å, α = 75.067(2), β = 67.838(2), γ = 69.165(2), V = 894.48(14) Å^3, Z = 1, 7913 reflections collected, 3059 unique (R_{int} = 0.0247). The final R was 0.1624 (all data) and wR was 0.3683 (all data).

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