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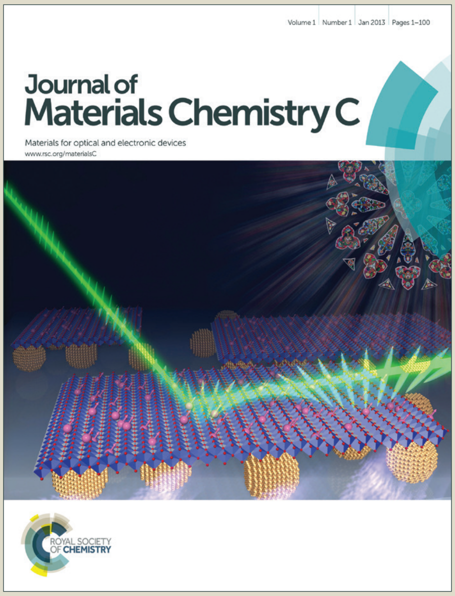

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ARTICLE TYPE

Thienyl Peripherally Substituted Rubrene Analogue with Constant Emissions and Good Film Forming Ability

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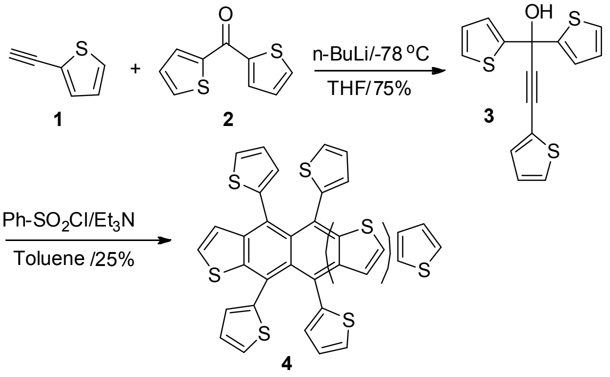
A new thienyl peripherally substituted rubrene analogue was synthesized. Different from rubrene quenching of fluorescence after aggregation, this compound emits constantly yellow-green light both in solution and in aggregation state. Meanwhile, this rubrene analogue exhibits better film forming ability with the hole charge carrier mobility up to 0.01 cm^2 V^{-1} s^{-1}.

As a benchmark of organic semiconductors, rubrene has been extensively studied both experimentally and theoretically.[1] Rubrene has found important applications in organic field effect transistors(OFETs) as an active layer[2] and organic light-emitting diodes (OLEDs) as a doping layer due to the high charge carrier mobility and the excellent electroluminescence respectively.[3] However, the high mobility of rubrene is mainly focus on the device fabricated by its crystal, the poor film forming ability limits its application;[4] on the other hand, although rubrene is highly fluorescent in its solutions, it becomes weakly luminescent along with the increase of concentration or aggregation in the solid state due to the formation of fluorescent quenching species such as exciplexes or excimers,[5] which prevents the use of rubrene in OLEDs as the active neat layer. Is it possible to design rubrene analogues or derivatives that not only improve the film forming ability but also eliminate the aggregation-caused quenching? Up to now, some derivatives of rubrene have been designed and syhthesized[6] by introducing halgon or alkyl group to rubrene, few of its analogue have been designed and synthesized.[7]

Very recently, by introducing two thienyl lateral group to the tetracene backbone of rubrene, we first obtained the orange light-emitting rubrene analogue with aggregation induced enhancement emission (AIEE) properties by keeping a distorted molecular conformation,[7a,8] confining the rotations and preventing the π···π stacking in the solid state.[9] In this report, by replacing the six peripheral phenyl units of rubrene with thienyl groups, we obtained a new rubrene analogue **4** with intense yellow-green fluorescence both in solution and solid state. To the best of our knowledge, this is the first rubrene analogue with almost constant intensity of fluorescence after aggregation. Moreover, the compound **4** showed much better film forming ability, leading to the hole charge carrier mobility up to 0.01 cm^2 V^{-1} s^{-1}, four orders of magnitude higher than that of rubrene using the same device fabrication conditions. Our results would shed light on the development of rubrene analogues or derivatives combining the light-emitting properties with charge transporting behaviours.

The two-step synthetic route for the compound **4** was shown in Scheme 1.[10] Firstly, thienylacetylene **1** reacted with dithienyl ketone **2** to give the intermediate product **3** in the yield of 75%. Secondly, the dimerization of compound **3** proceeded in the presence of benzene-sulfonyl chloride and triethylamine to give the two isomers of target product **4** in the yield of 25%, which is too difficult to separate due to the structure similarity.



Scheme 1 Synthetic route to compound **4**.

Firstly, the thermal stability of compound **4** and rubrene were measured under the same conditions (see supporting information Fig. S1). The onset decomposition temperature of compound **4** was 351 °C, which was higher than that of rubrene (324 °C).

The UV-vis absorption spectra of the compound **4** showed a well-defined vibronic fine structure of the S_0-S_1 transition, as shown in Fig. 1A. Because the thiophene substitution generally reduces the aromatic π-delocalization compared with the benzene counterpart for acene derivatives,[11] the maximum absorption edges of compound **4** is blue shifted by 67 nm, from 551 nm to 484 nm compared with rubrene. This is the reason why this compound is yellow in eye while rubrene and the other analogues is orange or red. The energy gaps for rubrene and compounds **4** are 2.25 eV and 2.56 eV, calculated by the onsets of absorption peaks.[12]

The redox properties of rubrene and compounds **4** were shown in Fig. 1B; their highest occupied molecular orbits (HOMO) levels were calculated to be -5.16 eV and -5.33 eV by the onsets of oxidation peaks, respectively. According to their energy gaps and HOMO levels, their LUMO levels were calculated to be -2.91 eV and -2.97 eV, respectively. Different with the other rubrene analogues, lower HOMO levels and broad energy gap leads to the higher stability of compound **4** than that of rubrene. The sulfur atom in thiophene rings supplies two π -electrons in the five-membered ring to complete the aromatic sextet and thus, isoelectronic hydrocarbons "phenes" for the respective classes are afforded by substituting the sulfur atom with two sp2 carbons. Compared with "acenes", "phenes" have low-lying HOMO and high-lying LUMO energy levels[13]. In addition, thiophene substitution slightly reduces the aromatic π-delocalization compared to the benzene counterpart; resulting in HOMO stabilization[14].Therefore the thinenoacences have lower HOMO (more positive oxidation potential) and higher LUMO level than acenes.

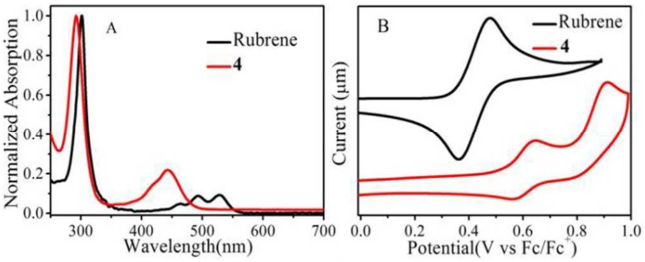


Fig. 1. UV-vis spectra (A) and cyclic voltammograms curves (B) of compounds **4** and rubrene. Both of them are measured in CH_2Cl_2 solution, using Fc/Fc^+ as the reference electrode.

Besides the lower HOMO levels and broad energy gaps, the improvement of the stability of the novel rubrene analogues also could be calculated by density functional theory (DFT). The DFT calculations of compound **4** and rubrene are performed with Gaussian03 at the B3LYP/6-31G (d) level (see supporting information Fig. S2).[15] The largest coefficients of rubrene (R) were mainly located on the tetracene core, while that of compounds **4** showed similar electronic structure in the tetracene core with moderate coefficient on thienyl rings, especially for the LUMO levels, which was presumably one important contribution to the stability.

Interestingly, different with rubrene, the fluorescence of compound **4** remained almost unchanged after aggregation from the solution to the solid state. The dilute solution of the compound **4** in THF was prepared while water was chosen as a nonsolvent of the dye to induce the aggregation behaviour.[16] As shown in Fig. 2, with the addition of water content, the intensity of fluorescent increased insignificantly, and the emission maximum wavelength of compound **4** showed a negligible shift from 528 nm to 532 nm. With the content of water increasing from 0 to 97 vol%, its PL intensity was only increased about 1.2-fold for compound **4**, which was measured at the same dye concentration under identical measurement conditions. When CH_2Cl_2 was used as solvent, hexane or methanol used as nonsolvent, respectively, similar results were obtained (see supporting information Fig. S3 and S4). When we chose rubrene as reference compound, the relative fluorescence quantum yield of compound **4** in solution was 80.5%. In solid state, the absolute fluorescence quantum yield of compound **4** was 7% while that of rubrene was lower than 1%. We can conclude that compound **4** is a constant photoluminescent material emitting yellow-green light.

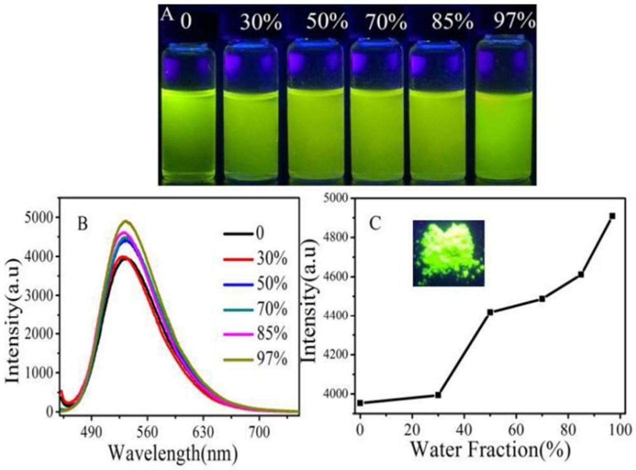


Fig. 2. (A) PL pictures of **4** solutions with different water fractions under UV (365 nm) light. (B) PL spectra of **4** in different water–THF (v/v) mixtures. (C) The dependence of the PL intensity on the composition of water (inset: luminescent photo of the solid powder under 365 nm). The concentration was kept at 40 μM, excitation wavelength: 442 nm.

To examine the film forming ability of compound **4**, the morphologies of vacuum-deposited thin films on the bare Si/SiO_2 substrates were investigated by atomic force microscopy (AFM). Fig. 3A and 3B shows the AFM images of films of compound **4** and rubrene on bare Si/SiO_2 substrate at 20 °C. The results showed that compound **4** formed a net-shape thin film on bare Si/SiO_2 substrates demonstrated that better thin films of compound **4** could be obtained on bare Si/SiO_2 substrates under vacuum deposition conditions, while rubrene thin films in which isolands formed and isolated from each other by large areas.[17] So we can conclude that compound **4** shown better film forming ability than that of rubrene on bare Si/SiO_2 substrates.

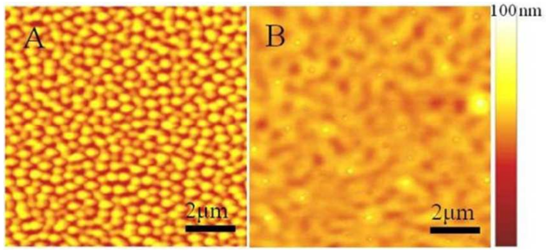


Fig. 3. AFM thin film images of rubrene (A) and compound **4** (B) at 20 °C on bare Si/SiO_2 substrate.

To investigate the field-effect properties of compound **4**, top-contact, bottom-gate of OFETs were fabricated by vacuum deposition (50 nm) on bare-Si/SiO_2 (300 nm SiO_2) substrates at room temperature. Copper mesh was chose as template for deposited gold electrodes, so all of the devices are in the same size (240μm in length and 30μm in width). Representative output and transfer curves at room temperature were shown in Fig. 4. The field-effect mobility (μ) in the saturated region and the threshold voltage (V_T) were calculated using the following eqn (1):[18]

$$I_{DS}= (W/2L)\, C_i\mu\, (V_G- V_T)^2 \qquad (1)$$

Where W and L are the channel width and length, respectively, C_i is the unit dimensional dielectric capacitance of gate insulator, μ is the field-effect mobility, and V_T is the threshold voltage. The estimated field-effect mobility, current on/off ratio (I_{on}/I_{off}) and threshold voltage (V_T) were 0.01 $cm^2\ V^{-1}\ s^{-1}$ (the average mobility was about 0.006 $cm^2\ V^{-1}\ s^{-1}$), 3.6×10^5, and -20 V, respectively. We also fabricated devices on thin film of rubrene, which exhibited much lower hole-mobility (~10^{-6} $cm^2\ V^{-1}\ s^{-1}$).

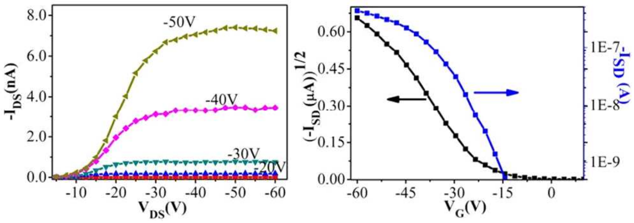


Fig. 4. Typical output (left) and transfer curve (right) of top-contact field-effect transistors based on vacuum-evaporated thin film of compound **4** on bare-Si/SiO_2 substrates.

In summary, we designed and synthesized a new thienyl peripherally substituted rubrene analogue. Different with rubrene, which emits orange light in solution and become weakly significantly in solid state, the compound emits yellow-green light both in solution and in aggregation state. To the best of our knowledge, this is the first report regarding rubrene with constant fluorescent intensity after aggregation. Moreover, this analogue showed much better film forming ability than that of rubrene. The highest hole mobility of OFET fabricated by compound **4** was up to 0.01 $cm^2\ V^{-1}\ s^{-1}$, thus paving the way to the development of rubrene analogues and derivatives used both in light-emitting and transistor devices.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis detail of compounds **4**, TGA of compounds **4**. For ESI or other electonic format see DOI: 10.1039/b000000x.

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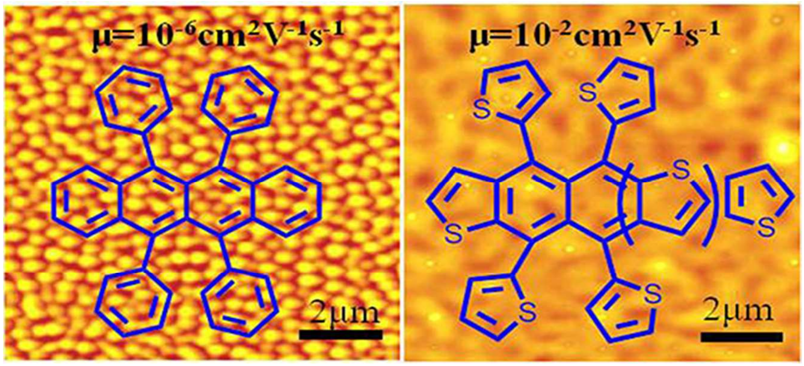
Graphical and textual abstract for “Thienyl Peripherally Substituted Rubrene Analogue with Constant Emissions and Good Film Forming ability”:



The rubrene analogue emits constantly yellow-green light and exhibits good film forming ability with the improved hole mobility.