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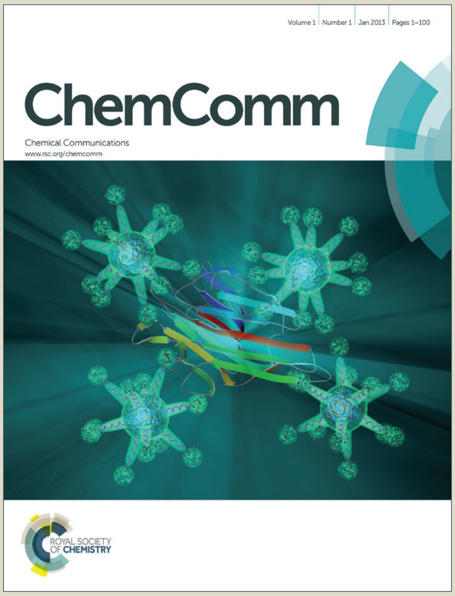

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ARTICLE TYPE

Charge Transfer (CT) Mechanochromism: Dramatic CT Absorption Change of Crystalline π-Conjugated Oligomers Containing TCNQ Upon Mechanical Grinding

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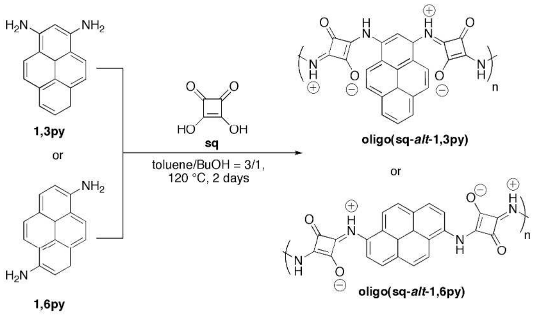
New π-conjugated oligomers with high crystallinity were prepared from the simple solvothermal reaction of squaric acid and diaminopyrenes. The oligomers were bonded at the 1,3- and 1,6-positions of the pyrene units, oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py), which greatly affected their planer configuration and resulting mechanochromic properties. Oligomers containing a charge transfer (CT) complex were selectively synthesized in one step. Upon mechanical grinding in the solid state, the color changed from orange to deep metallic green.

Recently, organic complexes with electron donor (D) and electron acceptor (A) moieties have emerged as promising candidates for advanced mechanochromic materials due to to their intramolecular charge transfer (CT) capability. This endows the materials with charge ordering, spin density waves (SDW), spin-Peierls ground state and superconductivity.[1] Aromatic molecules, such as coronene, are typical examples of π-electron systems able to donate electrons depending on their ionization potential *I.* As a typical example, 7,7,8,8-tetracyanoquinodimethane (TCNQ) can be easily reduced to form the open shell electron radical anion TCNQ$^{\cdot -}$ when it contacts with electron donors. Recently, a three-component system comprised of two different benzenoid hydrocarbons together with one molecule of TCNQ was repoted.[2] The pyrene-TCNQ complex was synthesized with molecular ratio 1 : 1 in toluene under refluxing conditions. Notably, the compound crystalized in a monoclinic system, with a space group $P2_1/n$ with half of the molecular of pyrene and TCNQ as the asymmetric part of the unit cell. The pyrene moiety is tilted with respect to the TCNQ along the stacks, with an angle between mean planes of 6˚. If this principle could be introduced into an oligomer ore polymer chain backbone, a force-sensitive CT complex as the chemical unit (mechanophore) would be linked into the polymer and oligomer backbones. Mechanical loading would then drive conversion of the mechanophore to a new chemical species. Therefore, we expect the possibility of completely alternating stacking for the CT complex between pyrene and TCNQ using mechanical grinding. The is to say, the mechanochromism[3] phenomenon will be observed, which is characterized by changes of color (absorption) *and/or* luminescence as a result of mechanical grinding or pressing of a sample in the solid state. Accordingly, the mechanical grinding of pyrene-TCNQ complexes in the solid state would lead to much higher increase of high CT complex absorption and the color of the grinded solid will change.

To create the system described above, we utilized the simple structure of squaramide, which is, typically synthesized *via* the stepwise reaction of commercially available squaric acid with amines and aromatic amines.[4] The hydrogen bond donor-acceptor properties of squaramide have attracted interest for various applications in supramolecular chemistry, e.g., as catalysts,[5] molecular sensors,[6] and in molecular recognition as receptor for charged guests.[7] Moreover, there is a growing number of bioactive squaramides involved in cancerous,[8] inflammatory[9] and infectious[10] diseases, among others.

Herein, we report the synthesis of π-conjugated squaric acid diamide-type oligomers composed of 1,3- or 1,6-diaminopyrenes and squaric acid with TCNQ (molecular ratio 1 : 1 : 1), oligo(sq-*alt*-1,3ampy) and oligo(sq-*alt*-1,6py). The obtained oligomers show bright orange colors in the solid state at room temperature. Upon mechanical grinding, oligo(sq-*alt*-1,6py) changes from orange to a deep green metallic color. In contrast, oligo(sq-*alt*-1,3py) does not change color upon mechanical grinding because of the inferior plane angle compared to mchanochromic oligo(sq-*alt*-1,6py).



Scheme 1 Synthesis of poly(sq-*alt*-Xpy); X = 1,3: poly(sq-*alt*-1,3-py) and X = 1,6: poly(sq-*alt*-1,6py).

Initially, the pyrene-conjugated squaramide oligomers were synthesized using solvothermal conditions through the condensation reaction of squaric acid and 1,3- or 1,6-diaminopyrene in toluene : *n*-butanol (3 : 1 by vol.) at 120 ℃ for 2 days (Scheme 1). The resulting precipitates were collected by filtration, washed with methanol and acetone, and dried at 100 ℃

under vacuum to provide the oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) as bright orange in 65 and 72% yields, respectively. When mixed solvents of *n*-butanol with other aromatic solvents, such as mesitylene and benzene, were used, the resulting solid showed lower yields and crystallinity.

The Fourier transform infrared (FTIR) spectra of oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) exhibited three vibration bands at 1503, 1523 and 1590 cm^{-1}, characteristic of squamide C=O bonds (see Fig S1 in ESI). Elemental analysis of oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) revealed that the H, C, and N contents for oligo(sq-*alt*-1,3py) were 3.34, 69.51, and 12.44%, respectively, and the H, C, and N contents for oligo(sq-*alt*-1,6py) were 3.22, 69.01, and 13.2%, respectively, which are close to the calculated values of 3.34, 68.24, and 13.26% expected for an infinite squaric acid 1,3- or 1,6-diamidepyrene conjugated oligomers.

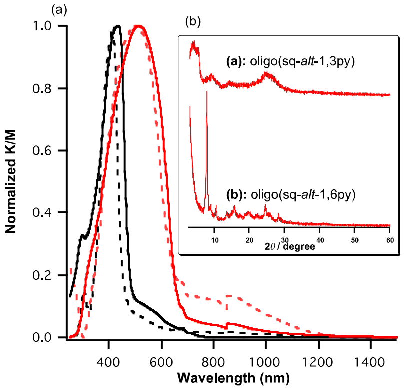
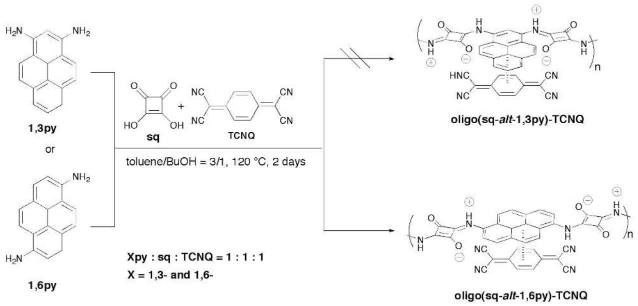


Fig 1 (a) Absorption spectra of the 1,3-diaminopyrene (block dotted curve), 16-diaminopyrene (black curve), oligo(sq-*alt*-1,3py) (red dotted curve), and oligo(sq-*alt*-1,6py) (red curve) and (b) PXRD profiles of oligo(sq-*alt*-1,3py) and oligo(sq-*al*t-1,6py).

UV-Vis absorption spectroscopy was used to evaluate the electronic properties of oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) relative to 1,3-diamiopyerene and 1,6-diaminopyrene (Fig. 1a). Both oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) (red curve) exhibited respective strong absorption bands at 527 and 530 nm, which were red-shifted by over 107 and 87 nm relative to those of 1,3-diamiopyerene (black dotted curve) and 1,6-diaminopyrene (back curve), respectively. The significant bathochromic shifts and extremely broad absorption bands of oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) suggest delocalization of the π electrons in the squaramide-pyrene oligomer backbone. Moreover, a slightly larger red-shift of oligo(sq-*alt*-1,6py) than that of oligo(sq-*alt*-1,3py) means that a squaraine unit connected at pyrene-1,6 position shows higher conjugation than that at pyrene-1,3 position. Thus the connection of the 1,6-position in pyrene unit leads to extended and larger π conjugation.

Powder X-ray diffraction (PXRD) measurements of oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) are shown in Fig.1b. The PXRD pattern of oligo(sq-*alt*-1,3py) has considerably broader weak peaks, which is characteristic amorphous structure containing crystalline objects. However, the XRD pattern of oligo(sq-*alt*-1,6py) displayed a strong sharp peak at 7.839° (11.2693 Å) and four weak peaks at 8.961 (9.8609 Å), 13.538 (6.5351 Å), 24.444 (3.6386 Å), and 25.920° (3.4347 Å).

To provide a more detailed understanding of the structure and photophysical behavior of oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py), we employedtheoretical calculations of model compounds using density-functional theory (DFT) and time-dependent DFT (TD-DFT) methods at the B3LYP/6-31G(d)/B3LYP/6-311G(d) level utilizing Gaussian 03 suite of programs.[11] The 1,3-connected model compound has a torsional structure in the 1,3-position of pyrene. In contrast, the 1,6-connected model compound shows high planarity, indicating that oligo(sq-*alt*-1,6py) possesses both higher crystallinity and larger extended π conjugation than the oligo(sq-*alt*-1,3py) (see Fig. S2 in ESI). The LUMO orbital is spread out down to the C=O and C-O^{-} groups of squaraine moiety in the 1,6-connected model compound although the orbital is not spread on their groups of 1,3-connected model compound. These result indicates that larger π conjugation of oligo(sq-*alt*-1,6py) is more extended than that of oligo(sq-*alt*-1,3py).



Scheme 2 the condensation of squaric acid and X-diaminopyrenes with TCNQ; X = 1,3: oligo(sq-*alt*-1,3py)-TCNQ and X = 1,6: oligo(sq-*alt*-1,6py)-TCNQ.

Next, we conducted the condensation reaction of squaric acid and 1,3- or 1,6-diaminopyrenes in the presence of TCNQ under same condition (Scheme 2) to afford the TCNQ-coordinated oligomers, oligo(sq-*alt*-1,3py)-TCNQ and oligo(sq-*alt*-1,6py)-TCNQ. The obtained solids were afforded in 54 and 78% yields, and were similar color to those of oligo(sq-*alt*-1,3py) and oligo(sq-*alt*-1,6py) (orange). The structures of the obtained oligomers were determined by FTIR spectroscopy (see Fig. S1 in ESI). Although oligo(sq-*alt*-1,3py)-TCNQ does not have the C=N band in the oligomer backbone, oligo(sq-*alt*-1,6py)-TCNQ showed a vibration band at 1789 cm^{-1}, assignable to TCNQ of a C=N bonds. Furthermore, elemental analysis of oligo(sq-*alt*-1,6py)-TCNQ revealed that the H, C, and N contents were 3.91, 71.84, and 11.45%, respectively, which are close to the calculated values of 3.91, 69.84, and 16.71% expected for an infinite CT-coordinated squaric acid 1,6-diamidepyrene conjugated oligomer. However, elemental analysis of the 1,3- conjugated oligomer was in poor agreement with that the of calculated values.

The CT complex formation in oligo(sq-*alt*-1,3py)-TCNQ and oligo(sq-*alt*-1,6py)-TCNQ was also confirmed by UV-Vis absorption spectroscopy (Fig. 2a). Although the oligo(sq-*alt*-1,3py)-TCNQ shows no CT band due to the torsional structure of squaraine moiety from the DFT calculation (Fig. S2 in ESI), the CT band of oligo(sq-*alt*-1,6py)-TCNQ was observed at 933 nm. According to XRD analysis, a strong peak of oligo(sq-*alt*-1,6py) at 7.839 ° disappeared. Four new sharp peaks of oligo(sq-*alt*-1,6py)-TCNQ appeared at 2.409 (36.6422 Å), 4.858 (18.1754 Å), and 5.322 (16.5902 Å), probably caused by the formation of a CT complex and hydrogen bonding interactions of sqaramide. The weak peaks at 23.735 (3.7457 Å), and 26.321° (3.3833 Å) were assigned to π-π stacking interactions, differing from the XRD pattern of the oligo(sq-*alt*-1,6py) (Fig. 2b). These data indicated that the condensation reaction of squaric acid and 1,6-diaminopyrene with TCNQ forms the oligo(sq-*alt*-1,6py) bearing the CT complex structure.

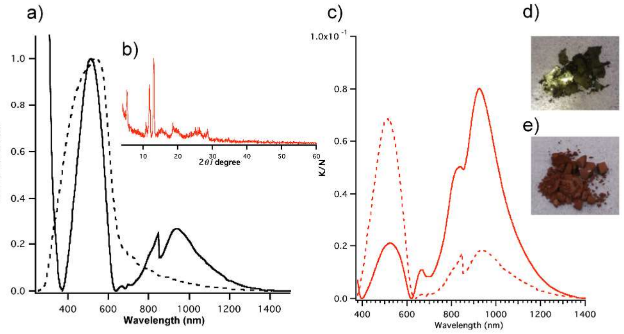


Fig. 2 (a) Absorption spectra of oligo(sq-*alt*-1,3py)-TCNQ (dotted curve), and oligo(sq-*alt*-1,6py)-TCNQ (block curve), (b) PXRD profiles of oligo(sq-*al*t-1,6py)-TCNQ, (c) grinding oligo(sq-*alt*-1,6py)-TCNQ (red curve) and gentl gound oligo(sq-*alt*-1,6py)-TCNQ (red dotted curve), d) grinding state, and e) ground sate.

The unique features of a oligo(sq-*al*t-1,6py)-TCNQ inspired us to explore the absorption response gained upon treating with mechanical force stimuli. We anticipated that interlayer interaction (hydrogen-bonding interactions of squaramide and π-π interactions) in the structure should change upon applying external force stimuli such as strong grinding. This should cause an increased CT complex absorption intensity of oligo(sq-*al*t-1,6py)-TCNQ.

When the crystalline oligomer bearing weak CT complex was treated with strong grinding in an agate mortar with a pestle, the color of oligo(sq-*al*t-1,6py)-TCNQ changed from orange to metallic deep green (Fig. 4b and c). From the measurement of UV-Vis spectra of oligo(sq-*alt*-1,6py)-TCNQ before and after grinding (Fig. 2c), when the pyrene absorption in oligo(sq-*alt*-1,6py)-TCNQ at 510 nm was decreased, the intensity of the CT complex absorption at 949 nm in oligo(sq-*al*t-1,6py)-TCNQ increased exceedingly. The intensity of grinding oligo(sq-*al*t-1,6py)-TCNQ in the XRD pattern was increased in the area of π-π stacking interaction at 23.735~28.644 ° (Fig S3). These results indicated that the crystalline oligo(sq-*al*t-1,6py)-TCNQ efficiently exhibited the mechanochromic phenomenon. From these results, we tried employing other acceptors such as a tetracyanobenzene (TCNB), which led to the same mechanochromic phenomenon by mechanical grinding (Fig. S4 in ESI).

In summary, we synthesized *π*-conjugated squaric acid diamide-type oligomers composed of 1,3- or 1,6-diaminopyrenes and squaric acid with TCNQ (molecular ratio 1 : 1 : 1), oligo(sq-*alt*-1,3ampy) and oligo(sq-*alt*-1,6py). The obtained oligomers exhibited bright orange color in the solid state at room temperature. The CT complex absorption color was strikingly changed from orange to metallic deep green color upon mechanical grinding, and could be recovered by sonication in toluene. Furthermore, this system was applicable to the use of other acceptors such as TCNB. This research reported herein, is the first example of mechanochromic metarials prepared by the introduction of CT complexes into π-conjugated oligomers.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Text giving typical experimental procedures data for all compounds, Fig. S1 showing IR spectra of all compunds, Fig.S2 showing the TD-DFT calculation of model compunds, Fig. S3 showing XRD pattern of oligomer before and after grinding, Fig. S4 showing UV and pthoto of mechanochromism using TCNB. See DOI: 10.1039/b000000x/

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