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Efficient modification of pyrene-derivative featuring third-order nonlinear optics via the click post-functionalization

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ABSTRACT

A series of pyrene derivatives featuring nonplanar structures of *N*,*N*-didodecylanilino-substituted donor and TCNE/TCNQ adduct acceptors have been efficiently synthesized via formal [2+2] cycloaddition. As the efficient click by TCNE and TCNQ, the products show strong charge-transfer (CT) bands in the visible (near-IR region), potent redox activities, and related photophysical properties. UV/vis spectra and electrochemical studies show that the CT properties of these systems are readily tunable by strong cyano acceptor introduction on the nucleophile, which have a larger effect on the lowest unoccupied molecular orbital (LUMO). In particular, compared with the adduct of TCNE, the product clicked with TCNQ possessed a stronger D–A conjugation and bulkier π spacers. The TCNQ product also has a larger third-order nonlinear optical property which was characterized by Z-scan experiments. This could point to potentially interesting applications of the new pyrene derivatives in optoelectronic devices and develop the new modification process for the design of different pyrene-based molecular electronic devices.

Introduction

The design of molecules for application in organic electronics is a multi-parameter challenge. The promising materials must involve both the optimization of the functional units and the combination of molecular and bulk properties suitable for the specific application.[1,2] π-Conjugated systems possess characteristically large electronic polarizabilities, and it is reasonable to expect conjugated molecules to possess substantial hyperpolarizabilities.[3,4] In addition, it has been generally accepted that donor and acceptor terminal sets separated by a π-conjugated system exhibit large $\chi(3)$ values.[5] This provides inspiration for the rational design of structural motifs that are promising for third-order nonlinear optics. There are many representative examples of conjugated materials, including symmetric polymethines, polyenes, and porphyrins.[6] However, the present conjugated nonlinear optical materials display several disadvantages such as complex fabrication and chemical instability. It is still significantly crucial to develop new nonlinear optical molecular with donor–acceptor (D–A)-substituted characteristics via simple and efficient routes.

Two major reasons that account for the superiority of pyrene are the significant formation of discotic chromophore leading to π-stacking and the tendency to form excimers, which seem to be a promising candidate for nonlinear optical materials. The presence of electron-rich or electron-poor units is important and permits the fine-tuning of the optical properties while also influencing the charge carrier mobility.[1] However, it is costly and time-consuming to make the modifications on the pyrene cores with a variety of energy levels due to the required tedious chemosynthesis and purification processes.

Innovative [2+2] cycloaddition of strong electron acceptors, such as tetracyanoethene (TCNE) and 7,7,8,8-tetracyano-quinodimethane (TCNQ) to electron-rich alkynes,[7,8] followed by retro-electrocyclization, provides efficient access to nonplanar push–pull chromophores featuring intense intramolecular charge-transfer (CT) and high third-order optical nonlinearities.[9] These transformations are generally fast, high-yielding, catalyst-free, 100% atom-economic, and the resulting products can be easily purified by precipitation or washing. Therefore, it is an admirable combination that develops a post-functionalization approach with alkyne-acceptor click chemistry aid of the synthesis of extraordinary pyrene derivatives.

Herein, we described such a reaction between TCNE/TCNQ and *N*,*N*-didodecylanilino (NNA)-substituted alkynes, giving access to a new class of low-molecular-weight pyrene derivatives revealing high third-order optical nonlinearities. Our approach opens a new platform of D-π-A systems that contained a centered acceptor and peripheral multidonors in contrast to conventional linear type

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of D-π-A compounds. They included NNA donor and 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) acceptor moieties, and were prepared by quite short and high-yielding synthetic routes. The novel and instructive examples of pyrene derivatives could become third-order nonlinear materials.

Materials and methods

Material details

All the reagents were purchased as reagent grade from commercial sources (Aldrich) and used without further purification. Triethylamine (TEA) and tetrahydrofuran (THF) were distilled and purged with argon before use. A Bruker DMS-400 spectrometer was used to record the ^{1}H NMR and ^{13}C NMR spectra at 298 K. $CDCl_3$ was the solvent for NMR and chemical shifts relative to tetramethyl silane (TMS) at 0.00 ppm are reported in parts per million (ppm) on the δ scale. The resonance multiplicity was described as s (singlet), d (doublet), and m (multiplet). MALDI-TOF negative ionization mass spectra were recorded on a Shimadzu spectrometer, using dithranol as matrix. Elemental analyses were performed at institute of chemistry Chinese academy of sciences, with a Flash EA 1112 instrument. All UV–visible spectra were recorded on a JASCO V-570 spectrophotometer. FT-IR spectroscopy was recorded on a Perkin Elmer LR-64912C spectrophotometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer Pyris 6 instrument.

Electrochemical tests

The redox properties of **PT**, **PTE**, and **PTQ** were investigated by cyclic voltammetry (CV) in CH_2Cl_2 (1×10^{-5} M, 0.1 M nBu_4NPF_6, all potentials versus the ferricinium/ferrocene couple (Fc^+/Fc)). Cyclic voltammetric (CV) measurements were carried out in a conventional three-electrode cell using Glassy Carbon working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled CHI 660C instrument at room temperature. The energy levels were calculated using the Ferrocene (Fc) value of −4.8 eV with respect to the vacuum level, which was defined as zero. The measured oxidation potential of Fc (vs Ag/AgCl) was 0.18 V. Therefore, the HOMO energy (E_{HOMO}) levels of the products could be calculated by the equation $E_{\mathrm{HOMO}} = e[E\mathrm{onset(ox)} - E_{1/2,\mathrm{Fc}} + 4.8\mathrm{V}]$ and the LUMO energy (E_{LUMO}) levels could be estimated by the equation $E_{\mathrm{LUMO}} = e[E\mathrm{onset(red)} - E_{1/2,\mathrm{Fc}} + 4.8\mathrm{V}]$, where $E_{1/2,\mathrm{Fc}}$ stands for the half-wave potential of Fc/Fc^+.[10]

Nonlinear optical measurements

The nonlinear optical properties' (NLO) response of molecular **PT**, **PTE**, and **PTQ** was measured by means of Z-scan technique, employing 20 ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser (EKSPLA PL2143B). The linearly polarized laser beam was focused with a 200 mm focal length lens and the sample was moved across the focus by means of a computer controlled micrometric translation stage. The beam waist at the focus was typically 20 ± 5 μm and the pulse energy, after suitable attenuation, was in the range 0.2–0.5 μJ. Z-scan is a relatively simple experimental technique allowing for the simultaneous determination of the real and imaginary parts of the third-order susceptibility $\chi(3)$.[11] All of the samples were measured at 10^{-6} M solution in tetrahydrofuran solvent (specpure). The solvent itself does not show any third-order nonlinearity under our experimental conditions.

Synthesis methods

4,4′,4″,4‴-(Pyrene-1,3,6,8-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(*N,N*-didodecylaniline) (PT)

To a degassed solution of dry Et_3N/THF (1:1, 15 mL), 1,3,6,8-tetrabromopyrene (as compound **1** in supporting information, 0.50 g, 0.97 mmol) and *N,N*-didodecyl-4-ethynylaniline (2.64 g, 5.82 mmol) were added and the mixture degassed under Ar. Catalytic agents $Pd(PPh_3)_2Cl_2$ (13.62 mg, 0.019 mmol) and CuI (7.39 mg, 0.039 mmol) were then added, and the reaction mixture was stirred overnight at 80 °C under Ar. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 6:1) to afford **PT** as an orange solid (1.33 g, 0.66 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (4H, s), 8.31 (2H, s), 7.53 (d, *J* = 8.4 Hz, 8H), 6.63 (d, *J* = 8.4 Hz, 8H), 3.29 (16H, m), 1.60 (16H, s), 1.28 (144H, m), 0.89 (24H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 132.6, 132.2, 130.5, 125.9, 124.0, 119.0, 110.9, 108.5, 96.9, 85.6, 50.5, 31.3, 29.0, 28.8, 26.6, 22.1, 13.6 ppm. FT-IR (KBr): 2923, 2853, 2192, 1607, 1592, 1519, 1459, 1375, 1261, 1184, 1066, 809 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{144}H_{222}N_4$: 2007.75 g mol^{-1}, found: 2009.5 g mol^{-1} $[MH]^+$. Elemental analysis calcd (%) for $C_{144}H_{222}N_4$ (2007.75): C 86.08, H 11.14, N 2.79; found: C 86.03, H 11.19, N 2.78

3,3′,3″-(8-(1,1,4,4-Tetracyano-3-(4-(didodecylamino)phenyl)buta-1,3-dien-2-yl)pyrene-1,3,6-triyl)tris(2-(4-(didodecylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile) (PTE)

TCNE (0.038 g, 0.30 mmol) was added to a solution of **PT** (0.10 g, 0.050 mmol) in dichloromethane (15 mL), and the mixture was stirred for one hour at room temperature. Evaporation of the solvent and column chromatography (silica gel; dichloromethane) afforded the desired products (0.11 g, 0.044 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 8.77 (4H, s), 7.97 (2H, s), 7.71 (8H, s), 6.71 (8H, s), 3.37 (16H, s), 1.62 (16H, s), 1.27 (144H, m), 0.85 (24H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 153.4, 132.4, 129.7, 125.4, 114.2, 112.9, 111.0, 110.5, 95.2, 67.9, 51.6, 31.8, 29.5_3, 29.4_7, 29.2, 27.3, 26.9, 25.5, 22.6, 14.0 ppm. FT-IR (KBr): 2925, 2853, 2215, 1602, 1533, 1492, 1417, 1340, 1292, 1184, 993, 809 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{168}H_{222}N_{20}$: 2519.80 g mol^{-1}, found: 2521.3 g mol^{-1} $[MH]^+$. Elemental analysis calcd (%) for $C_{168}H_{222}N_{20}$ (2519.80): C 80.02, H 8.87, N 11.11; found: C 80.12, H 8.79, N 11.09.

2,2′,2″,2‴-(1,1′,1″,1‴-(Pyrene-1,3,6,8-tetrayl)tetrakis(2-(4-(dicyanomethylene)cyclohexa-2,5-dienylidene)-2-(4-(didodecylamino)phenyl)ethan-1-yl-1-ylidene))tetramalononitrile (PTQ)

TCNQ (0.061 g, 0.30 mmol) was added to a solution of **PT** (0.10 g, 0.050 mmol) in dichlorobenzene (15 mL), and the mixture was stirred for one hour at 100 °C. Evaporation of the solvent under reduced pressure and column chromatography (silica gel; dichloromethane) afforded the desired products (0.13 g, 0.047 mmol, 94%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (4H, s), 7.71 (2H, s), 7.53 (8H, s), 7.27 (8H, s), 6.60 (16H, s), 3.30 (16H, s), 1.55 (16H, s), 1.24 (144H, m), 0.85 (24H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 151.7, 135.9, 134.9, 133.2, 130.2, 127.4, 125.2, 114.3, 112.7, 65.2, 51.3, 31.6, 29.3, 29.0, 27.2, 26.7, 22.3, 13.8 ppm. FT-IR (KBr): 2924, 2853, 2204, 1596, 1521, 1465, 1398, 1362, 1261, 1181, 1094, 802 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{192}H_{238}N_{20}$: 2823.92 g mol^{-1}, found: 2825.2 g mol^{-1} $[MH]^+$. Elemental analysis calcd (%) for $C_{192}H_{238}N_{20}$ (2825.2): C 81.60, H 8.49, N 9.91; found: C 81.75, H 8.36, N 9.89.