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PAPER

Structure, photophysics, and photooxidation of crowded diethynyltetracenes†

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This paper describes a previously unreported class of sterically crowded tetracene derivatives that have both phenyl and ethynyl substituents. The steric crowding above and below the tetracene core prevents overlap between the extended π-systems of the acenes. Substituent effects cause these tetra-substituted tetracenes to have absorbance and fluorescence spectra red shifted from either disubstituted derivatives or rubrenes, such that they have spectra similar to diarylpentacenes, but with higher quantum yields of fluorescence and greater photostability. These new molecules also undergo cycloaddition reactions with $^1O_2$, giving regioisomeric mixtures of endoperoxides, and in contrast to longer acenes, the ethynyl substituents show only a modest stabilizing effect to photooxidation. Ethynylated tetracenes also exhibited photochromism, with their endoperoxides undergoing cycloreversion to yield the acene starting material at room temperature in the dark.

Introduction

This paper describes the synthesis, optical properties, and cycloaddition reactivity of a previously unreported class of substituted tetracenes: 5,12-diethynyl-6,11-diphenyltetracenes. Linear acenes of three or more rings have important roles in a number of applications. Acenes are among the materials that have the best performance in organic electronics:[1] thin films of pentacene and single crystals of rubrene show efficient charge transport properties. Rubrene and other acenes are common luminescent materials in light-emitting devices[2] and in chemiluminescent glowsticks. In addition to their useful properties in devices, depending on their substitution, acenes can undergo facile cycloaddition reactions with dienophiles.[3–6] Cycloaddition reactions with singlet oxygen ($^1O_2$)[7,8] have been identified as a mechanism of acene degradation,[9] and also play a key role in schemes for sensing $^1O_2$ both from our group[10] and others.[11,12] Acene-based cycloaddition reactions with other dienophiles are also useful for constructing structural scaffolds such as iptycenes.[13]

Primary pathways of acene decomposition include endoperoxide formation with singlet oxygen and photodimerization. There have been a variety of substitution strategies to increase the stability of acene derivatives, including substitution with halogens,[9,14] thioethers,[15–17] sterically demanding arenes,[9] and heteroaromatics;[18] ethynyl substitution, however, such as in 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS pentacene) is among the most popular.[19–23] Silylethynyl groups have been critical in stabilizing large acenes, such as hexacene,[24,25] heptacene,[23,24] and nonacene[26] that are otherwise too reactive to isolate and characterize. Work on silylethynyl hexacenes has shown that for these longer acenes, dimerization, and not photooxidation, appears to be the primary mode of decomposition.[25] In addition, heptacenes that bear both silylethynyl and phenyl substituents are reported to be the most stable such derivatives.[23,27]

Ethynyl substitution red-shifts absorbance and luminescence spectra of acenes because of increased π-conjugation, and also improves solubility, which enables solution processing to replace vacuum deposition for constructing devices. Our group is interested in strategies for tuning both emission color and cycloaddition reactivity of acenes for applications in $^1O_2$ detection or photo-tunable solid-state emitters. The goal of this study was to develop soluble, red-emitting, $^1O_2$-reactive acenes that are significantly more stable than 6,13-diarylpentacenes, which are too reactive for reliable handling of thin films under typical laboratory conditions. Tetracenes are an interesting class of molecules for this purpose because they have reactivities and optical properties that are intermediate relative to similarly substituted anthracene and pentacene derivatives. A number of classes of substituted tetracenes have been reported, such as 5,12-diethynyltetracenes,[28,29] tetraalkyltetracenes,[30–32] dialkoxytetracenes,[33] and substituted rubrene derivatives.[34,35] Herein we report the preparation, photophysical properties, and reactivity of what we believe to be a new class of sterically crowded substituted tetracenes.

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Experimental section

General considerations

The following chemicals were purchased from commercial sources and used as received: 1,3-diphenylisobenzofuran (Acros), 1,4-naphthoquinone (Aldrich), 5,12-naphthacenequinone (Acros), 6,13-pentacenedione (TCI), phenylacetylene (Aldrich), 4-methoxyphenylacetylene (Alfa Aesar), Sn(II) chloride dihydrate (Alfa Aesar) and poly(9,9-di-n-dodecylfluorenyl-2,7-diyl) (Aldrich). Dry tetrahydrofuran (THF) was obtained using a column purification system.

All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230–400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Chemical shifts are reported relative to residual protonated solvent (7.27 ppm for $CDCl_3$). High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion.

Synthesis

General procedure for the synthesis of acene derivatives. n-Butyllithium (1.6 M) in hexanes was added to a solution of acetylene derivative in dry THF dropwise at −78 °C and stirred vigorously at room temperature for 20 min. The reaction mixture was then cooled to −78 °C and solid quinone was slowly added. The solution was then allowed to warm up to room temperature and stirred for 75 min before treatment with 10% HCl aqueous solution saturated with Sn(II) chloride dihydrate and extracted with dichloromethane. The crude product was purified *via* flash chromatography on silica gel using $CHCl_3$ and recrystallized from methanol and chloroform. 6,11-diphenyltetracene-5,12-dione was prepared by condensation between 1,3-diphenylisobenzofuran and 1,4-naphthoquinone. 5,12-bis(4-methoxyphenyl)tetracene was prepared as previously reported.[10]

5,12-Diethynyl-6,11-diphenyltetracene derivatives (1T–4T). 1T–4T were prepared according to the general synthesis procedure: 0.6 g (1.45 mmol) 6,11-diphenyltetracene-5,12-dione, 2.5 equivalents of ethynyl derivative, 2.2 mL (3.51 mmol) n-butyllithium in hexanes (1.6 M), 30 mL dry THF and 15 mL 10% HCl aqueous solution saturated with $SnCl_2$ dihydrate yielded the products after chromatography and recrystallization as described above.

1T (0.26 g, 31%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58–8.57 (m, 2H), 7.56–7.54 (d, 6H), 7.46–7.43 (t, 6H), 7.30–7.27 (m, 10H), 7.23 (s, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.3, 137.9, 134.3, 132.8, 131.7, 131.2, 128.6, 128.3, 128.1, 128.1, 128.0, 127.7, 127.2, 127.1, 125.8, 124.3, 119.1, 108.9, 89.7. HRMS calcd for $C_{46}H_{28}$ (M + H)$^+$, 581.2264; found, 581.2280.

2T (0.33 g, 35%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57–8.56 (m, 2H), 7.55–7.54 (d, 6H), 7.50–7.43 (m, 6H), 7.35–7.31 (m, 6H), 7.22–7.20 (m, 6H), 6.82–6.80 (d, 4H), 3.82 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 141.5, 137.9, 134.3, 133.2, 132.8, 131.2,

128.6, 128.2, 127.9, 127.7, 127.2, 126.9, 125.6, 119.2, 116.6, 113.7, 109.0, 88.7, 55.5. HRMS calcd for $C_{48}H_{32}O_2$ (M + H)$^+$, 641.2475; found, 641.2463.

3T (0.16 g, 16%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56–8.54 (m, 2H), 7.60–7.57 (m, 10H), 7.56–7.47 (m, 6H), 7.40–7.39 (d, 4H), 7.33–7.31 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.2, 137.9, 134.3, 132.8, 131.8, 131.4, 128.5, 128.4, 127.5, 127.2, 126.1, 125.1, 118.9, 107.3, 91.8. HRMS calcd for $C_{48}H_{26}F_6$ (M + H)$^+$, 717.2011; found, 717.2028.

4T (0.18 g, 17%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66–8.65 (m, 2H), 7.64–7.62 (m, 2H), 7.51–7.48 (m, 10H), 7.45–7.43 (m, 2H), 7.27–7.24 (m, 2H), 1.07 (s, 42H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.0, 137.5, 135.0, 133.2, 130.9, 128.6, 128.1, 128.0, 127.0, 126.7, 125.6, 119.4, 112.1, 105.3, 19.1, 12.2. HRMS calcd for $C_{52}H_{60}Si_2$ (M + H)$^+$, 741.4306; found, 741.4301.

5,12-Diethynyltetracene derivatives (1D–4D). 1D–4D were prepared according to the general synthesis procedure: 0.40 g (1.5 mmol) 5,12-naphthacenequinone, 3.0 equivalents of ethynyl derivative, 2.8 ml (4.5 mmol) n-butyllithium in hexanes (1.6 M), 20 mL dry THF and 12 mL 10% HCl aqueous solution saturated with $SnCl_2$ dihydrate yielded the products after chromatography and recrystallization as described above.

1D (0.32 g, 48%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29 (s, 2H), 8.69–8.67 (m, 2H), 8.12–8.09 (m, 2H), 7.85–7.82 (m, 4H), 7.58–7.55 (m, 2H), 7.49–7.46 (m, 8H).

2D (0.41 g, 54%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.28 (s, 2H), 8.70–8.69 (m, 2H), 8.10–8.08 (m, 2H), 7.80–7.78 (m, 4H), 7.57–7.55 (m, 2H), 7.49–7.44 (m, 2H), 7.04–7.02 (m, 4H), 3.92 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2, 133.4, 132.3, 132.2, 130.1, 128.8, 127.6, 126.6, 126.2, 126.0, 118.5, 116.0, 114.5, 103.5, 86.2, 55.6. HRMS calcd for $C_{36}H_{24}O_2$ (M + H)$^+$, 489.1849; found, 489.1853.

3D (0.45 g, 52%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.25 (s, 2H), 8.66–8.64 (m, 2H), 8.13–8.11 (m, 2H), 7.95–7.94 (m, 4H), 7.77–7.75 (m, 4H), 7.62–7.60 (m, 2H), 7.53–7.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.7, 132.5, 132.1, 130.1, 128.7, 127.4, 127.2, 126.6, 126.2, 125.8, 125.2, 123.1, 122.8, 118.4, 102.1, 89.5. HRMS calcd for $C_{36}H_{18}F_6$ (M + H)$^+$, 565.1385; found, 565.1396.

4D[28] (0.39 g, 43%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.31 (s, 2H), 8.64–8.62 (m, 2H), 8.03–8.01 (m, 2H), 7.56–7.54 (m, 2H), 7.48–7.46 (m, 2H), 1.33 (s, 42H).

6,13-Diethynylpentacenes (1P–4P). 1P–4P were prepared according to the general synthesis procedure: 0.40 g (1.3 mmol) 6,13-pentacenedione, 3.0 equivalents of ethynyl derivative, 2.4 ml (3.8 mmol) n-butyllithium in hexanes (1.6 M), 18 mL dry THF and 10 mL 10% HCl aqueous solution saturated with $SnCl_2$ dihydrate yielded the products after chromatography and recrystallization as described above.

1P[36] (0.33 g, 53%) ^{1}H NMR (500 MHz, $CDCl_3$): d 9.31 (s, 4H), 8.07–8.05 (m, 4H), 7.93–7.91 (m, 4H), 7.55–7.52 (m, 4H), 7.50–7.48 (m, 2H), 7.44–7.42 (m, 4H).

2P (0.32 g, 43%) ^{1}H NMR (500 MHz, $CDCl_3$): d 9.27 (s, 4H), 8.05–8.02 (m, 4H), 7.85–7.82 (m, 4H), 7.41–7.38 (m, 4H), 7.06–7.03 (m, 4H), 3.91 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) d 160.3, 133.4, 132.3, 130.37, 128.8, 126.3, 126.0, 118.2, 116.0, 114.5, 104.7, 87.0, 55.6. HRMS calcd for $C_{40}H_{26}O_2$ M$^+$, 538.1927; found, 538.1924.

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3P[37] (0.35 g, 44%) ^{1}H NMR (500 MHz, CDCl$_3$) d 9.29 (s, 4H), 8.10–8.08 (m, 4H), 8.03–8.02 (m, 4H), 7.81–7.80 (m, 4H), 7.48–7.46 (m, 4H).

4P[38] (0.33 g, 40%) ^{1}H NMR (500 MHz, CDCl$_3$): d 9.31 (s, 4H), 7.99–7.97 (m, 4H), 7.43–7.41 (m, 4H), 1.38 (s, 42H).

Optical experiments

Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Irradiation of the methylene blue photosensitizer to generate [1]O$_2$ was performed with a 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water filter, manual shutter, a 665 nm high-pass filter and a focusing plano-convex lens (focal length 15 cm) in the light path.

Kinetics

A stock solution of methylene blue was prepared in CHCl$_3$ to give an absorbance of 1.0 at its peak. Ethynyl derivatives (**1T–4T**, **1D–4D**, **4P**), 5,12-bis(4-methoxyphenyl) tetracene **5**, or 6,13-bis (4-methoxyphenyl) pentacene **6** was dissolved in CHCl$_3$ at a concentration of 0.005 M. 5,12-Bis(4-methoxyphenyl)tetracene **5** was used as reference for **1T–4T**, **1D–4D**, and 6,13-bis(4-methoxyphenyl) pentacene **6** was used as the reference for **4P**. When the 0.005 M solution was diluted 100-fold with the methylene blue stock solution, the final concentration of the acene in the sample was 0.05 mM. With the sample placed 15 cm from the light source, the solution was irradiated using a 665 nm high-pass filter and convex lens in increments of 15 s for 120 s (**1T–4T**) or increments of 45 s for 360 s (**1D–4D**, **4P**); the absorbance spectrum was measured after each interval of irradiation.

Synthetic photooxidation

The acene was dissolved in CDCl$_3$ with methylene blue and bubbled with O$_2$. The solution was irradiated with the Hg/Xe lamp using a high-pass filter and plano-convex lens. When all starting material has reacted, methylene blue was removed by quick filtration with silica gel in a filter funnel.

4T endoperoxides: HRMS calcd for C$_{52}$H$_{60}$O$_2$Si$_2$ (M + H)$^+$, 773.4205; found, 773.4190. **3D** endoperoxides: HRMS calcd for C$_{36}$H$_{18}$F$_6$O$_2$ (M + H)$^+$, 597.1284; found, 597.1298.

Crystal structure determination

Low-temperature diffraction data (φ-and ω-scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) from an IμS microsource. All structures were solved by direct methods using SHELXS[39] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[40] using established refinement techniques.[41] For details of data quality and structure refinement, see ESI.

Results and discussion

Synthesis of acenes

Fig. 1 shows the four derivatives of the diethynyldiphenylte-tracene core (tetra-substituted tetracenes, compounds with suffix "**T**") prepared, each with different terminal groups bound to the alkyne substituents. Cycloaddition between 1,3-diphenyliso-benzofuran and napthoquinone yielded the common diphenyl-tetracenequinone intermediate.[34,35] Addition of appropriately substituted acetylide anions, prepared by deprotonation of the terminal acetylene with n-BuLi, followed by reduction of the resulting diols with SnCl$_2$ gave the target acenes **1–4T**. Similar strategies, using commercially available tetracenequinone or pentacenequinone, gave analogously substituted 5,12-dieth-ynyltetracenes (**1D–4D**) and 6,13-diethynylpentacenes (**1P–4P**). Yields of the tetrasubstituted compounds were 15–35%, whereas those of the disubstituted compounds were somewhat higher. We ascribe the lower yield of the **T**-series compounds to steric hindrance presented by the terphenyl moiety on the quinone.

X-ray crystal structures

Single crystal X-ray structures of compounds **2T** and **4T** high-light the influence of the substituents on the structures of this new class of substituted acenes (Fig. 2 and 3). Both of these sterically crowded molecules relieve intramolecular congestion through structural distortions. In addition to all the phenyl substituents on the terphenyl moieties being rotated away from a conformation coplanar with the tetracene backbone, the substituents are bent away from each other, which has been observed in other tetra-substituted tetracenes.[28,35] The arylethynyl groups of **2T** are rotated out of plane by 73° and 66° in opposite directions, in contrast to less congested 5,12-diarylethynyltetracenes, in which the aromatic groups bound to the sp-hybridized carbons are coplanar with the acene backbone.[29] The bulkier triisopropylsilyl groups of **4T** force even greater distortions, with the tetracene backbone of **4T** having a significant twist of 31° (Fig. 3). This type of twisting is known to occur in single crystals of sterically congested acenes.[42] We suspect that in solution the acene back-bone of **2T** may also be twisted, but that crystal packing forces planarize the tetracene in the single crystal, as is known for rubrene.[43] **4T** crystallizes in the chiral space group $P2_12_12_1$ with
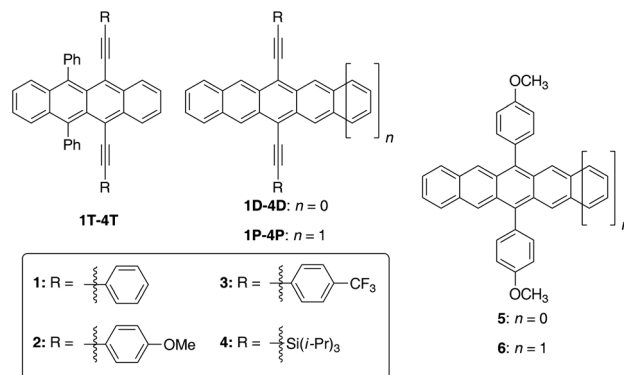

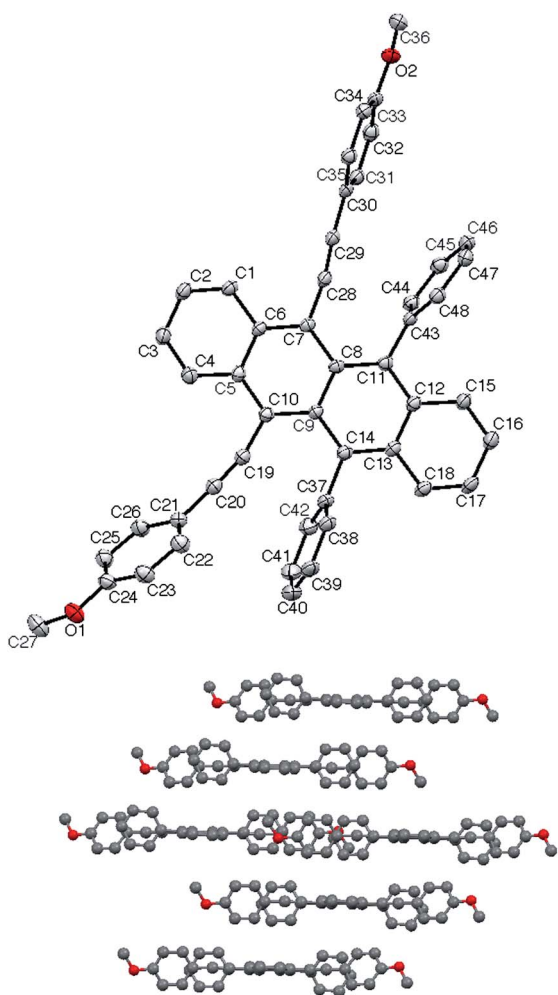**Fig. 1** Structures of acenes studied in this work.

Fig. 2 X-ray crystal structure of **2T** with atomic labeling scheme. Hydrogen atoms omitted for clarity. Thermal ellipsoids shown at 50% probability. Packing diagram visualized in a projection along tetracene cores.

Fig. 3 X-ray crystal structure of **4T**. Methyl groups omitted from lower structure for clarity. Ellipsoids shown at 50% probability.

only one of the two possible twisted enantiomers present in the crystal we analyzed.

Although **2T** shows interactions between the anisyl rings in neighboring columns along the crystallographic *a*-axis, neither **2T** nor **4T** exhibits significant π–π interactions between the acene backbones in their crystal structures. Steric hindrance presented above and below the acene plane by the twisted arene rings prevents such interactions. The closest to such an interaction is a distance of 4.63 Angstroms between parallel mean planes defined by the tetracene ring systems of **2T**. The pitch between these molecules is so large, however, that the distance between centroids of the tetracenes is 7.02 Å (Fig. 2).

Photophysical properties

Table 1 summarizes absorbance and fluorescence parameters for all tetracenes investigated; the trends discussed below comparing **2T** and **2D** are consistent with the other pairs of similarly substituted acenes. Fig. 4 contrasts the absorbance and fluorescence spectra of tetrasubstituted tetracene **2T** and with two related substituted acenes—5,12-dianisylethynyl tetracene (**2D**)
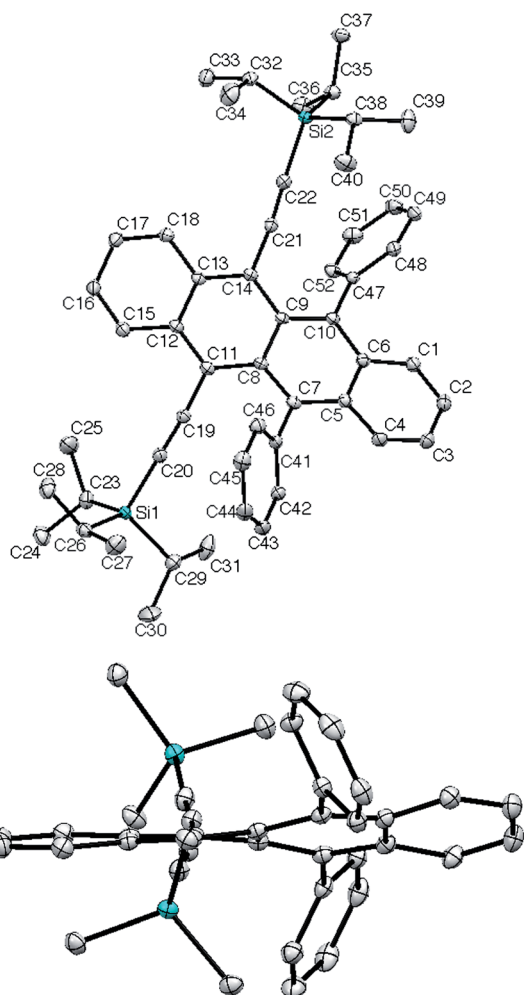
and 6,13-dianisylpentacene (**6**)—in dilute dichloromethane solution. Relative to the disubstituted tetracene **2D** that does not have pendant phenyl rings, compound **2T** shows a 30 nm red shift (587 nm *vs.* 557 nm, 0.12 eV lower energy) in the peak of the lowest energy vibronic band of absorbance, and a ∼50 nm (0.16

Table 1 Key properties of tetracene derivatives described in this paper[a]

	λ_{max} (ab)[b]	λ_{max} (em)	Φ_F[c]	k_{rel}[d]
1T	578 nm	616 nm	0.73	0.39
2T	586 nm	626 nm	0.63	0.30
3T	577 nm	625 nm	0.71	0.26
4T	575 nm	602 nm	0.75	0.40
1D	552 nm	565 nm	0.76	0.31
2D	559 nm	575 nm	0.85	0.40
3D	556 nm	571 nm	0.87	0.18
4D	534 nm	542 nm	0.67	0.23

[a] All photophysical data collected in CH_2Cl_2; kinetics data collected in $CHCl_3$. [b] Wavelength of maximum absorbance of the 0,0 band. [c] Measured relative to cresyl violet in methanol ($\Phi_F = 0.54$) or Coumarin 6 in ethanol ($\Phi_F = 0.78$). [d] Rate of reaction, relative to **5**, with $^1O_2$ prepared by irradiation of methylene blue in the presence of O_2.
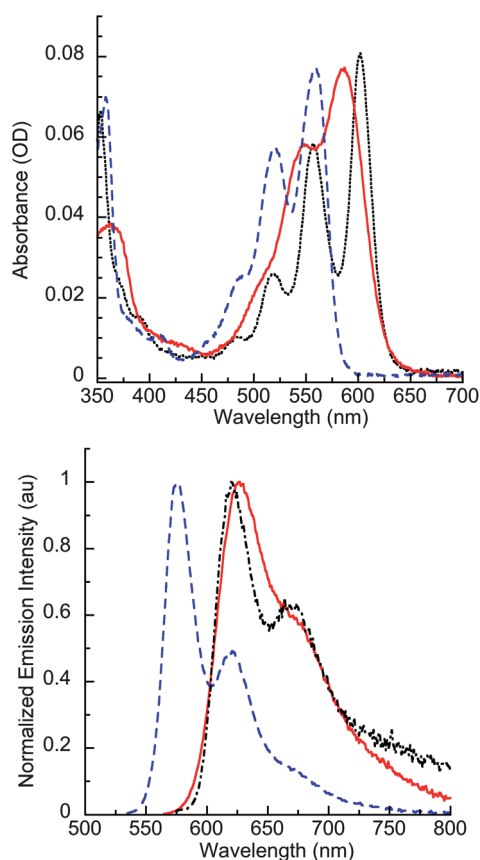
Fig. 4 Absorbance (top) and photoluminescence (bottom) spectra of **2T** (red solid lines), **2D** (blue dashed lines), and **6** (black dotted lines) in CH₂Cl₂. Phenyl substitution on **2T** red-shifts the absorption and emission spectra such that they resemble that of pentacene **6**.

eV) shift in the onset of absorbance. This red shift, resulting from the two additional phenyl rings substituted on the tetracene backbone, is analogous to that between 5,12-diphenyltetracene (494 nm) and rubrene (528 nm). Recent theoretical calculations on tetracene and rubrene have attributed this bathochromic shift upon substitution with phenyl rings to a destabilization of the HOMO by inductive effects from the phenyl rings and twisting of the tetracene backbone.[44] In addition, similar to rubrene, the absorbance spectrum of **2T** shows less vibronic resolution than **2D**, and a larger Stokes Shift, consistent with additional vibrational modes involving rotations of the phenyl substituents.[44] The optical HOMO–LUMO gap of **2T** is similar to **6** (1.9 eV), a highly reactive pentacene derivative, derivatives of which have been used as red emitters in light-emitting devices.[45]

The fluorescence spectrum of **2T** and related acenes in CH₂Cl₂ follows a similar pattern to that found in absorbance (Fig. 4): it is strongly red-shifted from most other previously reported tetracene derivatives, including **2D**, and has a maximum wavelength of emission (626 nm) similar to **6** (620 nm). We attribute these effects on the optical properties of **2T** to a combination of the extended π-conjugation from the phenylethynyl substituents and the inductive effects of the phenyl rings, which because of steric interactions are nearly orthogonal to the tetracene core. The emission spectra of **4T** and **4D**, which do not have aromatic rings bound to the alkyne substituents, are blue shifted from similar

structures that have arylethynyl substituents, consistent with reduced delocalization in molecules with fewer conjugated π-bonds. Increased conjugation from ethynyl groups also accounts for the red shifted absorbance and fluorescence that all of the **T**-series compounds described here have relative to rubrene.[43] All four of the tetrasubstituted tetracenes described here are highly fluorescent, with quantum yields of fluorescence (Φ_F) > 0.6, while Φ_F of **6** is 0.24. When doped into a host thin film of poly(9,9-didodecylfluorene) at 20% loading (w/w), **2T** accepted energy from the photoexcited host to give a ratio of emission intensities of 6 : 1 (guest:host, see ESI). The spectrum of the emissive acene in this film was nearly identical to that observed in solution.

¹O₂-mediated oxidation of tetracenes

Ethynyl substituents have been the most popular method for stabilizing pentacenes and higher-order acenes that are otherwise susceptible to photooxidation. To quantitatively evaluate the effect of alkynes on the photooxidation of these tetracenes, we determined the relative rates of reaction of these acenes with ¹O₂. Each acene, at a concentration of 5.0×10^{-5} M in air-equilibrated CHCl₃, was exposed to ¹O₂ by irradiation of the sensitizer methylene blue (MB) with a peak absorbance of 1.0 using a 200 W Hg/Xe lamp and a 665 nm high-pass filter. These conditions insured that MB was the only chromophore in solution absorbing any incident light. Control experiments in the absence of MB showed no reaction of acenes under otherwise identical irradiation conditions.

Table 1 summarizes the results of these experiments. Each reaction with photogenerated ¹O₂ followed pseudo first-order kinetics; the slopes of best-fit lines to plots of ln(absorbance) *vs.* time (Fig. 5) gave relative rate constants k_{rel}. The previously reported 5,12-dianisyltetracene (**5**) was the standard ($k_{rel} = 1$) for these kinetics experiments.[10] All of the ethynylated tetracenes (**T** and **D**) derivatives react with ¹O₂ with similar relative rate constants that are 2.5–5 times slower than diaryltetracene **5**. Trifluoromethyl-substituted derivatives **3T** and **3D** were the least reactive of each of their respective classes (**T** or **D**) of tetracenes.[27] This structure-property relationship is consistent with the
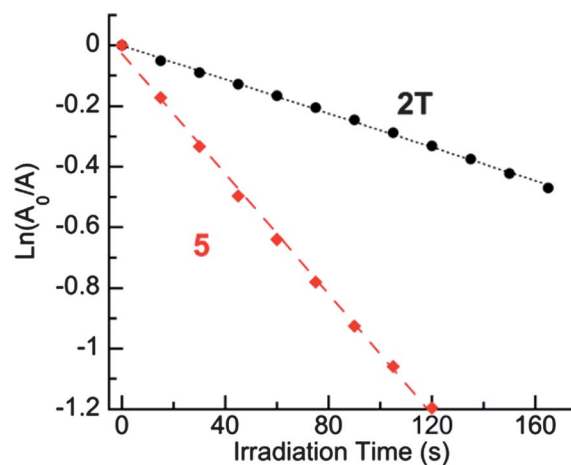

Fig. 5 Semilogarithmic kinetic plots showing relative rates of reaction of **5** (red diamonds) and **2T** (black circles) as a function of irradiation time of MB in air-equilibrated CHCl₃.
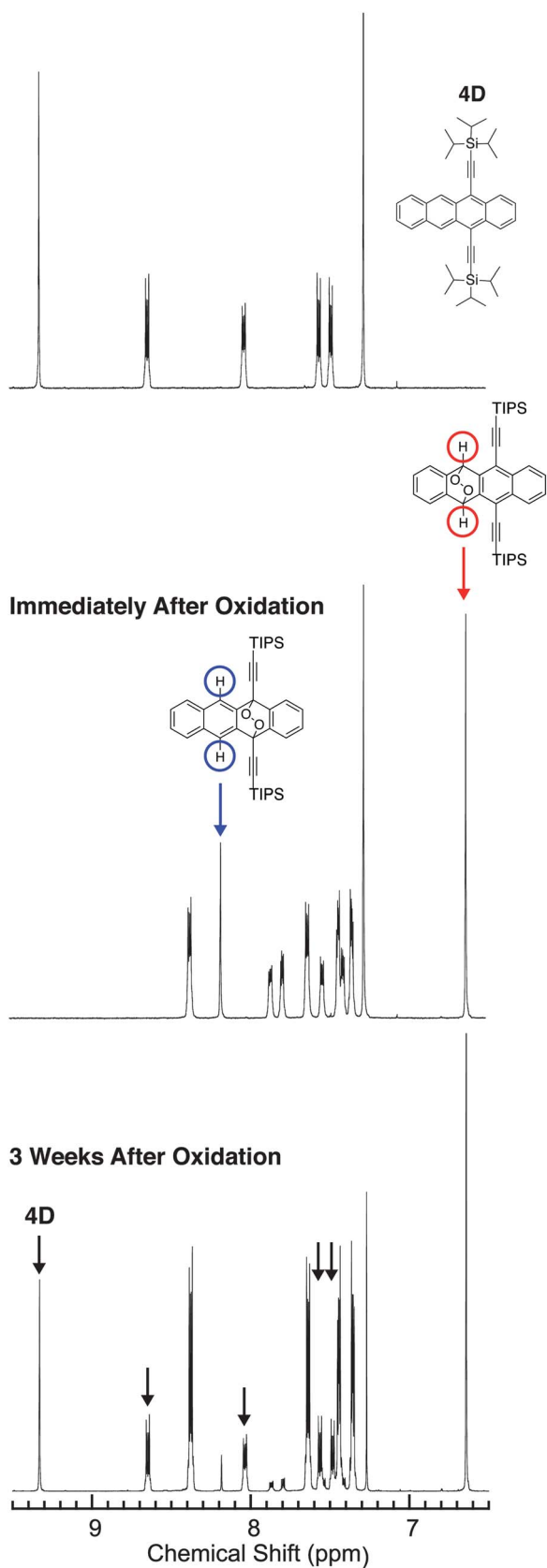
findings of both Chi and Ong, who used 4-trifluoromethylphenyl substituents to improve the stability of a heptacene and a pentacene, respectively, and attributed these observations to a lowering of the energy of the HOMO.[27,37]

Although there was some reduction in reactivity between these ethynylated tetracenes compared to non-ethynylated tetracene **5**, consistent with the electron withdrawing alkyne groups decreasing the reactivity of acenes towards $^1O_2$, the magnitude of this difference in stability towards photogenerated $^1O_2$ is one order of magnitude less than that reported for the difference in photolytic stability between 6,13-diphenylpentacene and TIPS-pentacene (**4P**).[9] Therefore, the ethynyl groups on TIPS-pentacene have a greater stabilizing effect than the ethynyl groups on these tetracenes. In addition, there was no statistically significant stabilization of any of the ethynyl-substituted tetracenes described here compared to **5** upon direct irradiation at λ > 400 nm in the absence of MB.

These observations are consistent with the conclusions of Maliakal, who found that the principal reason for stabilization of ethynylated pentacenes is the selective stabilization of the pentacene LUMO. These lower energy LUMOs result in low triplet energies, making them slow to donate energy to O_2, and make photoinduced electron transfer from the excited acene to O_2 less energetically favorable.[46,47] Tetracene derivatives have a larger band gap and higher energy LUMO than larger acenes. We therefore propose that unlike similarly substituted pentacene derivatives, the triplet energies of these ethynylated tetracenes are not of low enough energies to either prevent $^1O_2$ sensitization or accept energy from $^1O_2$, resulting in only a modest stabilization towards photooxidation relative to non-ethynylated tetracene **5**. The reported observation of the endoperoxide of silylethyne-substituted anthradithiophenes (ADTs),[48] together with an only slight increase in stability to photooxidation that these substituents provide to the ADT backbone,[36] is consistent with the proposed model.

Regioselective reversibility of $^1O_2$ cycloaddition

Analytical data of products of MB-mediated photooxidation of the tetracenes were consistent with mixtures of endoperoxides. For **D**-series tetracenes, ^1H NMR spectra showed clean mixtures of two endoperoxides, with characteristic singlets from bridgehead (δ 6.6 ppm) and aromatic protons (δ 8.2 ppm) corresponding to $^1O_2$ cycloaddition across the unsubstituted and ethynylated positions, respectively (Fig. 6).[49] Therefore, although there was a modest 2 : 1 regiochemical preference for oxidation of the unsubstituted position, silyl acetylenes did not protect ethynylated positions from photooxidation.[23] **T**-series compounds did not have these clearly identifiable characteristic NMR signals because of the high degree of substitution on the acenes; nevertheless, high resolution mass spectra (HRMS) of their products of oxidation by photosensitization with methylene blue were consistent with endoperoxides.

Cycloreversion of endoperoxides of tetracene derivatives typically requires heating or irradiation with short wavelengths

Fig. 6 NMR spectrum of **4D** (*top*), its products of photooxidation by methylene blue-mediated $^1O_2$ photosensitization (*middle*) in CDCl₃, and the same sample three weeks later, showing cycloreversion of the

endoperoxide substituted across the ethynylated positions; vertical arrows signify NMR signals assigned to **4D** formed *via* cycloreversion.

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of light.[50,51] In contrast, isolated mixtures of ethynylated tetracene endoperoxides developed the red color of the acene starting material upon storage in the dark, neat, under otherwise ambient conditions. In addition, for the one acene that we investigated in detail (**4D**, selected for the ease of NMR peak assignments), there was a large difference in the rate of the cycloreversion for the two endoperoxide regioisomers: the endoperoxoide on the ethynylated positions underwent cycloreversion, while it appeared that the other regioisomer was unreactive. The ^{1}H NMR spectrum of the endoperoxides of **4D**, which initially showed a 2 : 1 molar ratio of the two endoperoxides (as shown in Fig. 6), showed approximately 10% conversion to the acene and a 3 : 1 ratio of endoperoxides after four days in the dark. After three weeks, the ratio of endoperoxides was 20 : 1, with the endoperoxide on the unsubstituted positions the major regioisomer present, and the unoxidized acene representing about 25% of the molecules in the sample. No peaks other than those readily assigned to the endoperoxides or the acene were observed. This observation is consistent with a recent report by Fudickar and Linker, who found that endoperoxides of 9,10-diethynylanthracenes gave $^1O_2$ through cycloreversion on a short time scale.[52] We suspect that a transition state with propargyl radical character is responsible for the cycloreversion of the reactive regioisomer.[50,52,53]

Conclusions

We have prepared new sterically congested tetracene derivatives with absorbance and fluorescence similar to diarylpentacenes, but that are more efficient emitters and more resistant to photooxidation while still retaining sensitivity to $^1O_2$. We anticipate that the steric congestion around the tetracene core of the **T** series compounds, as reflected in the lack of acene-acene interactions in their crystal structures, should prevent "butterfly" dimerization,[25,54] which would otherwise be a source of false positives in $^1O_2$-responsive materials. Research into applications of these acenes in $^1O_2$-responsive materials, including reversibly responsive materials enabled by their photochromism, is currently under way in our laboratory.

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