**COMMUNICATION**

# Acene-Linked Conjugated Polymers with Ratiometric Fluorescent Response to $^1O_2$

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**This communication describes new conjugated polymers that bear diarylanthracene or diaryltetracene pendants and respond to singlet oxygen by interrupting energy transfer resulting in blue-shifted fluorescence.**

10 Fluorescent conjugated polymers (CPs) have applications in emerging technologies such as sensors,[1] organic light-emitting displays,[2] and photovoltaic devices.[3,4] These technologies harness the ability of CPs to conduct excitons, holes, and electrons. CP sensors rely on intra- and inter-chain exciton mobility to amplify 15 fluorescence quenching or energy transfer in response to specific analytes, such as single-stranded DNA,[5-7] nitroaromatics,[8,9] or oxidants such as hydrogen peroxide.[10] This amplifying property of CPs increases their sensitivity over comparable small molecule fluorescent sensors, which makes CPs exceptional sensing 20 materials, including for sensing of biological analytes.[11-13]

We are interested in developing CPs that respond specifically to analytes that can be amplified chemically. Singlet oxygen $(^1\Delta_g)$,[14,15] which has been used as a chemical trigger in chemiluminescence-based bioassays,[16,17] is generated readily by 25 triplet energy transfer from excited dye molecules to $O_2$.[18] In addition, $^1O_2$ is an important reactive oxygen species in photodynamic therapy and has been implicated in the genotoxicity of UV light.[19,20] A number of molecules that sense $^1O_2$ specifically through changes in intensity of fluorescence, phosphorescence, or 30 chemiluminescence have been reported.[21-26] These examples often comprise a luminescent dye linked to a $^1O_2$-reactive quencher (an anthracene derivative); upon [4+2] cycloaddition, quenching slows dramatically to allow observation of fluorescence of the dye. To our knowledge, CPs designed to respond to $^1O_2$ have not been 35 reported. In this communication, we describe fluorescent CPs substituted with linear fused acenes that respond to $^1O_2$ in a ratiometric manner through interruption of energy transfer pathways.

Our $^1O_2$-responsive conjugated polymers comprise a 40 poly(phenylene-*co*-fluorene) backbone and a $^1O_2$-reactive linear acene bound *via* an insulating four-carbon linker. The pendant acenes are acceptors in an energy transfer process with the CP backbone. We anticipated that the linear acene would: i) alter the emission of the CP backbone through electron transfer, energy 45 transfer, or both, and ii) undergo a [4+2] cycloaddition with $^1O_2$ to shut these pathways down and restore CP backbone fluorescence (Scheme 1).
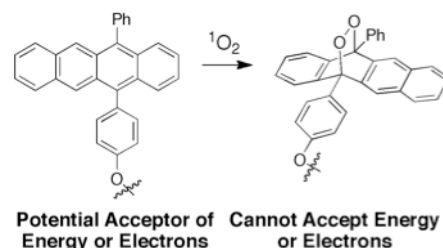


**Scheme 1.** Interruption of linear acene conjugation *via* cycloaddition of $^1O_2$ with diaryltetracene. Only one of two regioisomeric products is shown.
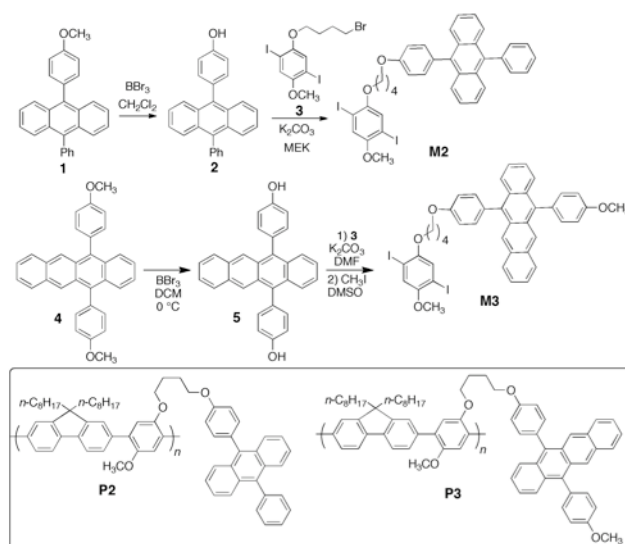


**Scheme 2.** Synthesis of acene-linked diiodo monomers and structures of resulting conjugated poly(fluorene-*co*-phenylene)s **P2** and **P3**.

In addition to a CP that contained only octyloxy chains on the phenylene rings with no $^1O_2$-reactive linear acenes (**P1**), we 50 prepared $^1O_2$-responsive CPs **P2** and **P3** (Scheme 2). Suzuki coupling between 9-bromo-10-phenylanthracene[27] and 4-methoxyphenylboronic acid gave anisyl-substituted anthracene **1**, which we demethylated with BBr3 to yield phenol **2**. Alkylation of **2** with known[28] monomer precursor **3** gave the anthracene-55 functionalized diiodo monomer **M2**. Synthesis of tetracene-substituted CP **P3** followed a different strategy, which involved addition of 4-methoxyphenyllithium to 5,12-napthacenequinone followed by reduction to the fully aromatized dianisyltetracene **4**,
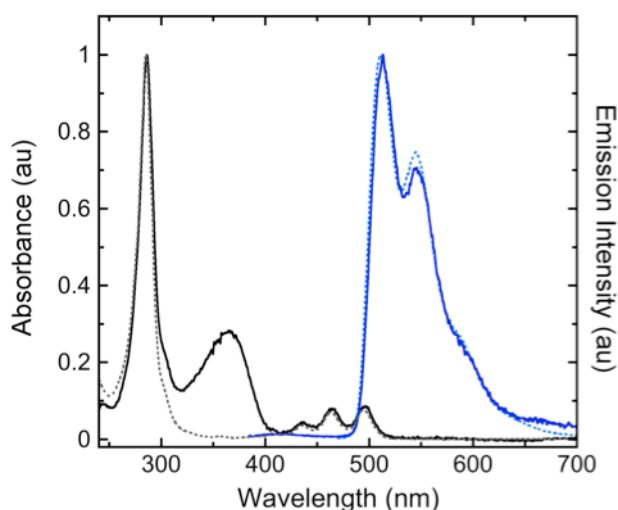
**Figure 1.** Normalized UV/vis (*left*, black lines) and fluorescence (*right,* blue lines) spectra of **P3** (solid lines) and 5,12-dianisyltetracene **4** (dotted lines).

deprotection of the methoxy groups, and stepwise alkylation of the resulting diphenol **5** with **3** and $CH_3I$ gave tetracene-containing diiodo monomer **M3**. Step-growth Suzuki polymerizations of **M2** or **M3** with commercially available 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester using standard biphasic conditions [$Pd(PPh_3)_4$, $K_2CO_3$, toluene/water, phase transfer catalyst, 90 °C] gave the target polymers **P2** and **P3**. These polymers had number average molecular weights ($M_n$) of 10,000-13,000 g/mol as determined by size exclusion chromatography versus polystyrene standards after precipitation into methanol and Soxhlet extraction with hexanes.

Figure 1 shows the electronic absorbance and fluorescence spectra of **P3** (solid lines) in dichloromethane, as well as that of the small molecule model tetracene **4** (dotted lines). The absorbance spectrum of **P3** contains both the characteristic bands of tetracene derivatives (a sharp band at 283 nm and the well-resolved vibronic bands between 400 and 500 nm) as well as a broad featureless band between 300 and 400 nm characteristic of poly(fluorene) derivatives. No bands appear in the UV/vis spectrum of **P3** that are not present in the spectra of the individual chromophores (**4** and **P1**), which indicates that there are no significant ground-state interactions between the polymer backbone and the pendant tetracene. In addition, the anthracene-substituted polymer **P2** shows similar characteristics, with the difference that the vibronic bands of the anthracene pendant overlap strongly with the absorption of the polymer backbone.

In contrast to differences between their absorbance spectra, **P3** and tetracene **4** show nearly complete overlap of emission spectra, with maxima at 512 nm (~ 100 nm red-shifted from **P1**). This overlap occurred whether the excitation wavelength excited the polymer backbone (373 nm) or the tetracene pendant. In addition, the excitation spectrum of **P3** resembles its UV/vis spectrum. This evidence taken together strongly supports the conclusion that efficient energy transfer takes place from the polymer backbone to the tetracene pendant groups. The significant overlap between the backbone emission ($\lambda_{max}$ = 417) and the tetracene absorbance between 410 and 510 nm also supports this conclusion.

Covalent linkage between these two chromophores is necessary

for energy transfer to occur in solution: when each component (**P1** and **4**) was dissolved in the same solution in an equimolar (per polymer repeat unit) ratio, fluorescence from **P1** dominated upon excitation at 373 nm. Anthracene-substituted polymer **P2** participated in analogous intramolecular energy transfer from the CP backbone to the pendant, although the effect was subtler because of the small difference in emission maxima between the pendant and the backbone (5 nm).

To examine the response of these molecules to $^1O_2$, we irradiated the photosensitizer methylene blue (MB) in a $CH_2Cl_2$ solution containing the fluorophore(s) of interest. MB generates $^1O_2$ with a quantum yield of ~ 0.5,[29] is soluble in organic solvents, and has an absorbance band that is strongly red-shifted ($\lambda_{max}$ = 654 nm) from the molecules and polymers studied here, which allows for its selective irradiation using a 590 nm high pass filter. Upon exposing model acenes **1** and **4** to identical conditions of $^1O_2$ photogeneration, the bimolecular rate constant for cycloaddition (as determined by the dependence of UV/vis spectra on irradiation time)[30] for tetracene **4** was 20 times faster than for anthracene **1** in
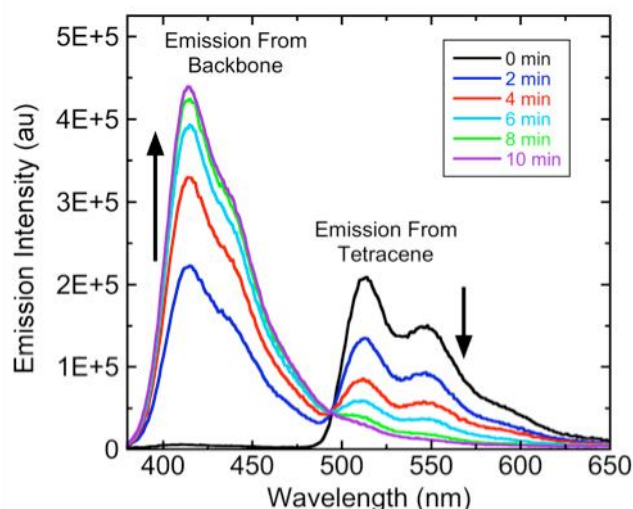


**Figure 2.** Ratiometric fluorescence response of **P3** in $O_2$-saturated $CH_2Cl_2$ as a function of time of irradiation of methylene blue.

$CDCl_3$. It is known that longer linear acenes generally react faster *via* cycloaddition with $^1O_2$ than similarly substituted shorter acenes.[31] NMR analyses of these reactions on a preparative scale in $CDCl_3$ were consistent with the endoperoxides as the products of these reactions.

We observed two key changes in the optical spectra of tetracene-substituted **P3** upon exposure to photogenerated $^1O_2$. First, the tetracene-based absorbance bands at 283 nm and between 410 and 510 nm decreased in intensity (ESI). Second, the tetracene emission at 510 nm decreased, while polymer backbone emission at 417 nm increased (Figure 2). The absorbance of the CP backbone at 365 nm did not decrease during exposure to $^1O_2$. The initial rate of reaction of **P3** with $^1O_2$ was of the same order of magnitude (two times smaller) as the rate of reaction between tetracene **4** and $^1O_2$ (Table 1). Although **P2** had a qualitatively similar response to photogenerated $^1O_2$, the shift in emission spectra was 5 nm, and the rate of reaction was slower, as expected from the studies with small molecules. The rate of reaction between **P2** and $^1O_2$ was slow enough to allow observation of

significant decomposition of the CP backbone.[32]

**Table 1.** Fluorescence maxima, quantum yields, and relative rates of $^1O_2$ cycloaddition of acene-linked polymers and small molecule acenes.

|  | $\lambda_{max}$ (emission) | $\Phi_F$ | $k(^1O_2)$ (relative) |
|---|---|---|---|
| **1** | 422 nm | 0.60 | 1 |
| **P2** | 422 nm | 0.58 | 0.6 |
| **4** | 512 nm | 0.64 | 21 |
| **P3** | 512 nm | 0.44 | 10 |

These observations are consistent with formation of the tetracene-endoperoxide. Tetracene and rubrene are known to form endoperoxides in high yield *via* $^1O_2$ cycloaddition.[33,34] Upon endoperoxide formation, energy transfer is no longer competitive with fluorescence from the CP backbone. Two negative control experiments were conducted: i) irradiating a solution of **P3** at λ > 590 nm in the absence of MB, and ii) allowing a solution containing MB and **P3** to remain in the dark. Both experiments showed no appreciable change in optical spectra. Finally, the $^1H$ NMR of **P3** showed changes consistent with endoperoxide formation upon exposure to $^1O_2$. The tetracene resonance at 8.3 ppm disappeared while a characteristic bridgehead resonance at 6.1 ppm appeared.

In conclusion, we have developed new acene-linked CPs that respond to $^1O_2$ through interruption of an energy transfer pathway by cycloaddition of the analyte with energy accepting linear acenes. To our knowledge, this is the first example of a conjugated polymer designed to respond to $^1O_2$. These materials have a ratiometric response, which can improve quantitative analysis through internal referencing.[35,36] In addition, the fluorescence enhancement of **P3** is against a dark background, which yields a large contrast (200-fold) in fluorescence intensity between "off" and "on" states. These characteristics are important for the development of fluorescent assays with these materials. We anticipate that an amplified response to $^1O_2$ should be possible by optimizing the stoichiometry of the reactive pendant. Ongoing work is focused on determining the specificity of the response, demonstrating this effect with solid-state CPs, and developing $^1O_2$-mediated assays.

## Notes and references

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