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COMMUNICATION

Acene-linked conjugated polymers with ratiometric fluorescent response to $^1O_2 \dagger$

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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.

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 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 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 triplet energy transfer from excited dye molecules to O₂.¹⁸ In addition, ¹O₂ 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 ¹O₂ specifically through changes in intensity of fluorescence, phosphorescence, or chemiluminescence have been reported.21-26 These examples often comprise a luminescent dye linked to a $^{1}O_{2}$ -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 ¹O₂ have not been reported. In this communication, we describe fluorescent CPs substituted with linear fused acenes that respond to ¹O₂ in a ratiometric manner through interruption of energy transfer pathways.

Our ${}^{1}O_{2}$ -responsive conjugated polymers comprise a poly(phenylene-*co*-fluorene) backbone and a ${}^{1}O_{2}$ -reactive



Scheme 1 Interruption of linear acene conjugation *via* cycloaddition of ${}^{1}O_{2}$ with diaryltetracene. Only one of two regioisomeric products is shown.

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 transfer, or both, and (ii) undergo a [4 + 2] cycloaddition with ${}^{1}O_{2}$ to shut these pathways down and restore CP backbone fluorescence (Scheme 1).

In addition to a CP that contained only octyloxy chains on the phenylene rings with no ${}^{1}O_{2}$ -reactive linear acenes (**P1**), we prepared ${}^{1}O_{2}$ -responsive CPs **P2** and **P3** (Scheme 2). Suzuki coupling between 9-bromo-10-phenylanthracene²⁷ and 4-methoxyphenylboronic acid gave anisyl-substituted



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

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Fig. 1 Normalized UV/vis (*left*, black lines) and fluorescence (*right*, blue lines) spectra of **P3** (solid lines) and 5,12-dianisyltetracene **4** (dotted lines) in CH_2Cl_2 .

anthracene 1, which we demethylated with BBr3 to yield phenol 2. Alkylation of 2 with $known^{28}$ monomer precursor 3 gave the anthracene-functionalized dijodo 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, deprotection of the methoxy groups, and stepwise alkylation of the resulting diphenol 5 with 3 and CH₃I 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(PPh₃)₄, K₂CO₃, toluene/water, phase transfer catalyst, 90 °C] gave the target polymers P2 and P3. These polymers had number average molecular weights (M_n) of 10000–13000 g mol⁻¹ as determined by size exclusion chromatography versus polystyrene standards after precipitation into methanol and Soxhlet extraction with hexanes.

Fig. 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 (\sim 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 support 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. Anthracenesubstituted 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 ${}^{1}O_{2}$, we irradiated the photosensitizer methylene blue (MB) in a CH₂Cl₂ solution containing the fluorophore(s) of interest. MB generates ${}^{1}O_{2}$ 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 ${}^{1}O_{2}$ 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 $CDCl_3$. It is known that longer linear acenes generally react faster via cycloaddition with ¹O₂ than similarly substituted shorter acenes.³¹ NMR analyses of these reactions on a preparative scale in CDCl3 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 ${}^{1}O_{2}$. First, the tetracene-based absorbance bands at 283 nm and between 410 and 510 nm decreased in intensity (ESI†).



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

Table 1 Fluorescence maxima, quantum yields, and relative rates of ${}^{1}O_{2}$ cycloaddition of acene-linked polymers and small molecule acenes

	$\lambda_{\rm max}$ (emission)/nm	$arPhi_{ m F}$	$k_{\rm rel} ({}^1{\rm O}_2)$
1	422	0.60	1
P2	422	0.58	0.6
4	512	0.64	21
P3	512	0.44	10

Second, the tetracene emission at 510 nm decreased, while polymer backbone emission at 417 nm increased (Fig. 2). The absorbance of the CP backbone at 365 nm did not decrease during exposure to ${}^{1}O_{2}$. The initial rate of reaction of **P3** with ${}^{1}O_{2}$ was of the same order of magnitude (two times smaller) as the rate of reaction between tetracene **4** and ${}^{1}O_{2}$ (Table 1). Although **P2** had a qualitatively similar response to photogenerated ${}^{1}O_{2}$, 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 ${}^{1}O_{2}$ was slow enough to allow observation of significant decomposition of the CP backbone.³²

These observations are consistent with formation of the tetracene-endoperoxide. Tetracene and rubrene are known to form endoperoxides in high yield *via* ${}^{1}O_{2}$ 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 $\lambda > 590$ 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 ${}^{1}O_{2}$. 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 ¹O₂ 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 ¹O₂. 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 the 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 ${}^{1}O_{2}$ 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 ¹O₂-mediated assays.

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