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Two-Photon Photosensitized Production of Singlet Oxygen: Sensitizers with Phenylene−Ethynylene-Based Chromophores

Sean P. McIlroy,[†] Emiliano Cló,[†] Lars Nikolajsen,[‡] Peter K. Frederiksen,[†]
Christian B. Nielsen,[†] Kurt V. Mikkelsen,[*,‡] Kurt V. Gothelf,[*,†] and Peter R. Ogilby[*,†]

Department of Chemistry, University of Aarhus, DK-8000 Århus, Denmark, and
Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark

kmi@theory.ki.ku.dk; kvg@chem.au.dk; progilby@chem.au.dk

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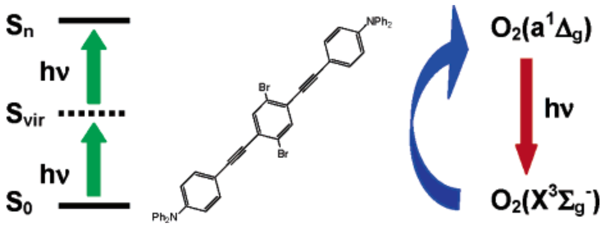

Singlet molecular oxygen ($a^1\Delta_g$) has been produced and optically monitored in time-resolved experiments upon nonlinear two-photon excitation of photosensitizers that contain triple bonds as an integral part of the chromophore. Both experiments and ab initio computations indicate that the photophysical properties of alkyne-containing sensitizers are similar to those in the alkene-containing analogues. Most importantly, however, in comparison to the analogue that contains double bonds, the sensitizer containing alkyne moieties is more stable against singlet-oxygen-mediated photooxygenation reactions. This increased stability can be advantageous, particularly with respect to two-photon singlet oxygen imaging experiments in which data are collected over comparatively long time periods.

Introduction

The lowest excited electronic state of molecular oxygen, singlet molecular oxygen ($a^1\Delta_g$), is an intermediate in many oxidation reactions.[1,2] In many systems of practical importance, these reactions occur in samples that contain heterogeneous, phase-separated domains.[3,4] Thus, for work in such systems, it could be of great use to both produce and detect singlet oxygen in time- and space-resolved experiments.

Singlet oxygen can be efficiently produced upon irradiation of a sensitizer which, in turn, transfers its energy of excitation to ground-state oxygen ($X^3\Sigma_g^-$).[5] Sensitizers can be a chromophore inherent to a given system, as is the case with many functional polymers.[6] Alternatively, a sensitizer can be specifically added to a system, as in the case of photodynamic therapy where light is used as a tool to selectively kill biological cells (e.g., cancer cells).[7]

Until recently, sensitizer excitation has always been achieved via a linear one-photon transition between the sensitizer ground state, S_0, and a singlet excited state of the sensitizer, S_n.[5] After excitation, singlet oxygen is most efficiently produced upon oxygen quenching of the sensitizer triplet state, T_1, formed upon intersystem crossing, $S_1 \rightarrow T_1$.[5]

It has been demonstrated, however, that singlet oxygen can also be produced upon nonlinear two-photon excitation of a sensitizer.[8−11] In this case, an excited-state S_m

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[*] To whom correspondence should be addressed.

[†] University of Aarhus.

[‡] University of Copenhagen.

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is populated as a consequence of the less-probable simultaneous absorption of two lower energy photons. The transition proceeds via a virtual state, $S_0 \rightarrow S_{vir} \rightarrow S_m$, and follows selection rules that can differ from those for a one-photon transition.[12] An important aspect of this approach is the opportunity to selectively populate an excited state at the point of a focused laser beam where a spatial domain of sufficiently high fluence can be obtained. In short, two-photon excitation of a sensitizer with a focused laser imparts spatial resolution to a singlet oxygen experiment.

We have embarked on a program to develop techniques by which singlet oxygen images of heterogeneous materials can be produced.[13−17] In one approach, we exploit the spatial resolution available through a two-photon, photosensitized excitation scheme combined with the time-resolved detection of singlet oxygen phosphorescence ($a^1\Delta_g \rightarrow X^3\Sigma_g^-$).[16] Because the singlet oxygen phosphorescence signal is extremely weak, however, a limiting aspect of this method is the need to acquire data over long periods of time. Under these circumstances, where the sample is exposed to prolonged irradiation, photooxygenation reactions can bleach the sensitizer which, in turn, adversely influences the production of singlet oxygen. It would thus be useful to develop stable sensitizers that produce singlet oxygen in high yield and that have a comparatively large two-photon absorption probability (i.e., large values of the so-called two-photon absorption cross section).

A critical component of a chromophore designed to absorb light in the UV−vis region of the spectrum, either by a one- or two-photon process, is a framework of conjugated π bonds. This framework not only plays a pivotal role in establishing transition energies (i.e., wavelengths of absorption) but facilitates the intramolecular charge redistribution associated with the development of transition moments, the magnitudes of which determine the transition probability. For many common chromophores, the network of conjugated π bonds often contains one or more alkenyl residues. Unfortunately, these double bonds can be quite susceptible to reactions with singlet oxygen, particularly if they are electron rich.[18] In light of this latter statement, attempts to make these double bonds less reactive toward singlet oxygen, and hence make the chromophore more stable, include the addition of electron-withdrawing substituents to the alkenyl moiety.[6]

Another option by which one might be able to appreciably stabilize a singlet oxygen sensitizer would be to incorporate alkyne rather than alkene-containing residues into the chromophore. In this case, one would try to capitalize on the general fact that alkynes can be significantly less reactive than the corresponding alkene with respect to electrophilic reagents.[19] Indeed, with respect to singlet oxygen in particular, alkynes are remarkably unreactive, certainly in comparison to the corresponding alkene. To our knowledge, singlet oxygen has been shown to react with alkynes in only two cases. In the first, the substrate was an amine-substituted alkyne (*N*,*N*-diethyl-1-propynylamine) and, hence, was particularly electron rich.[20] In the second, the alkyne was strained as a consequence of being incorporated in a ring.[21]

A substantial amount of work has been done in the recent past on the development of chromophores that have large two-photon absorption cross sections,[22,23] including the development of chromophores that contain ethynyl moieties.[24−28] With respect to the latter, it has indeed been noted that replacement of a double bond by a triple bond leads to improved photostability of the chromophore.[24] Most of the molecules produced, however, are highly fluorescent and are thus not well suited for the production of singlet oxygen. For the present study, we set out to explore issues pertinent to the development of two-photon chromophores containing ethynyl moieties that not only produce singlet oxygen in appreciable yield but that are stable upon prolonged exposure to singlet oxygen.

Results and Discussion

Molecules examined as singlet oxygen sensitizers are shown in Schemes 1−3. In our system of nomenclature, the subscript T identifies molecules that have a triple bond as an integral part of the chromophore, whereas the subscript D identifies molecules that contain a double bond. In addition to considering “rodlike” molecules (i.e., $\mathbf{3_T(X)}$ and $\mathbf{3_D(X)}$), in which photoinduced changes in charge distribution will principally be dipolar and/or quadrupolar in nature, we also examined a series of “tripodal” molecules (i.e., $\mathbf{1_T(X)}$ and $\mathbf{1_D(X)}$) in which changes in charge distribution can have an octupolar component. The two-photon behavior of a variety of octupolar mol-

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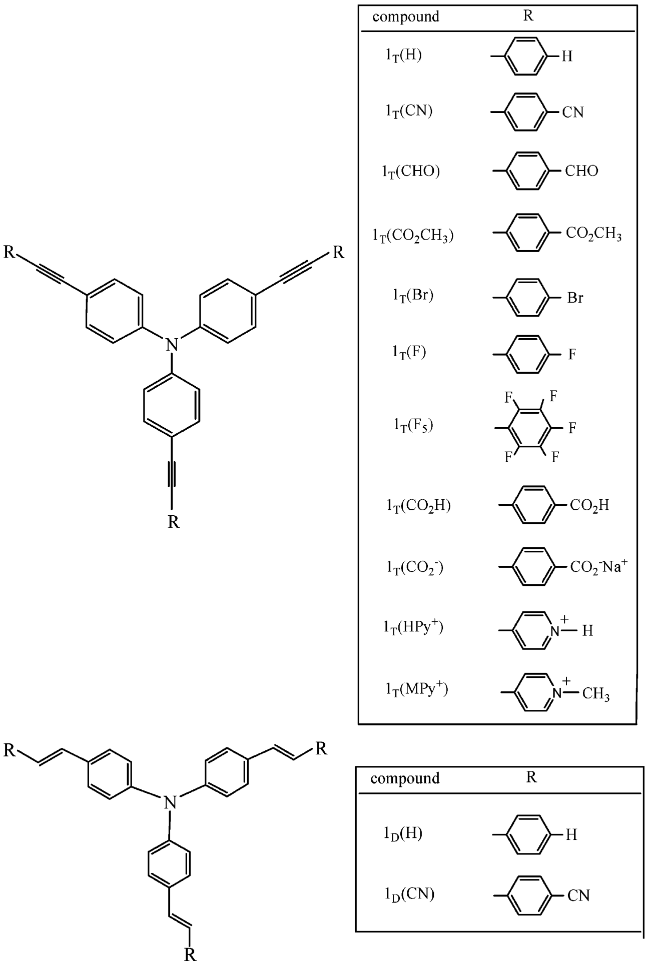
SCHEME 1



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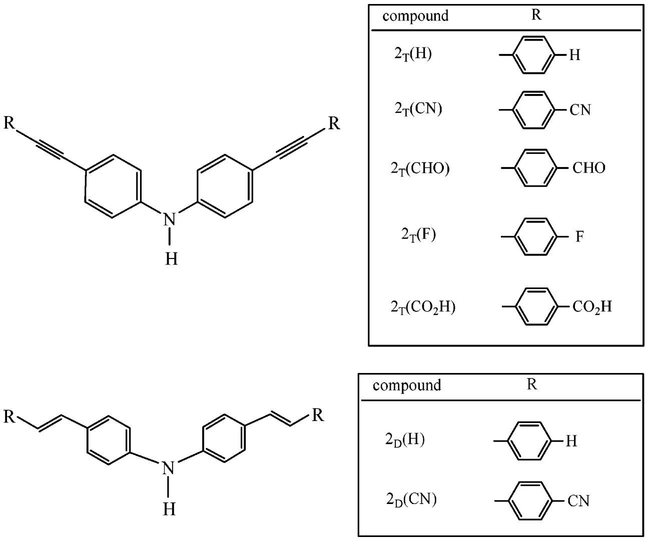
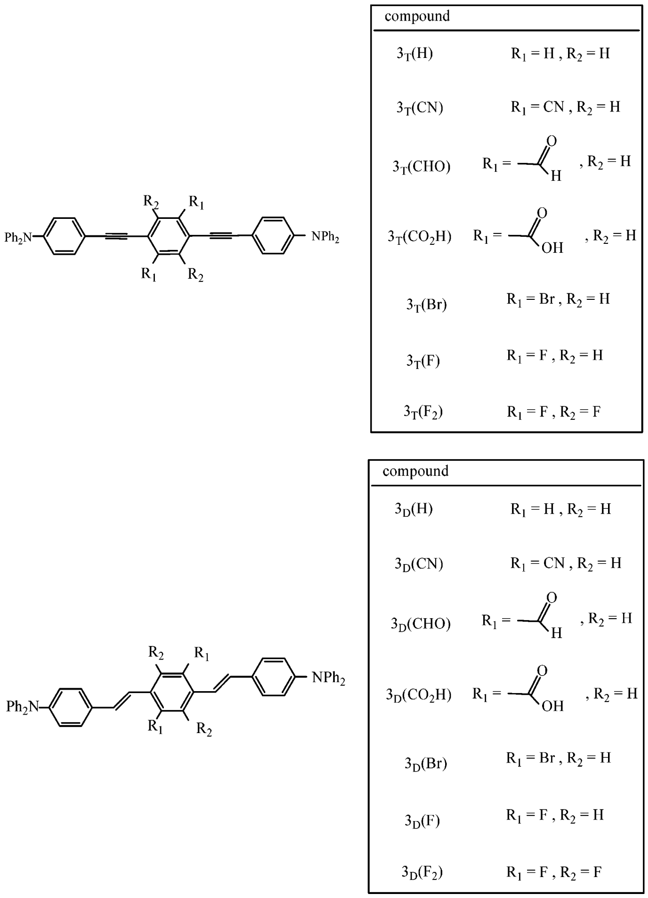


ecules has recently been examined by a number of groups.[28−32]

SCHEME 3



Computations. It has been demonstrated, both through our own work[9,10,33] as well as through the work of others,[34,35] that ab initio computations based on response theory can yield relatively accurate two-photon absorption cross sections for comparatively large polyatomic systems. From our perspective, such computations have become indispensable, not just as an aid in the interpretation of experimental data, but as a tool to predict which molecules are likely to be worth the often extensive efforts required for their synthesis and for making photophysical measurements.

For the present study, we set out to examine several conjugated π systems that are either known to be, or that could be, reasonable singlet oxygen sensitizers. Of general concern was the extent to which two-photon absorption cross sections would be influenced by (1) the change from an alkene to an alkyne moiety in the chromophore and (2) a change in substituents attached to the chromophore.

A. Alkene vs Alkyne Moieties in the Chromophore. Our computations indicate that, for a given pair of molecules, two-photon absorption cross sections for the alkyne-containing analogue are not significantly

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different from those for the alkene-containing analogue (Table 1). Second, the computations indicate that a given transition in the alkyne-containing analogue will generally be blue-shifted relative to the corresponding transition in the alkene-containing analogue. This latter point is further discussed below in the context of our spectroscopic measurements.

B. Substituent Effects. For the molecules examined in this study, our computations indicate that a change in the substituent attached to the chromophore can have a pronounced effect on the magnitude of the two-photon absorption cross section. This is indeed to be expected since the substituent's ability to either donate or accept electron density will influence the extent to which charge can be redistributed in the chromophore which, in turn, will influence the magnitude of the transition moment. However, for any two substituents, the relative effect of a change in substituent in the alkene-containing chromophore is essentially the same as that in the alkyne-containing chromophore. This suggests that, in the development of the transition moment, alkene-mediated intramolecular charge transfer does not significantly differ from alkyne-mediated charge transfer.

In conclusion, our computations indicate that if one has an established chromophore with desirable nonlinear optical properties, replacing alkene moieties with alkyne moieties should not have a significant adverse influence on the two-photon behavior of the system.

Synthesis. On the basis of our computational results, selected molecules were synthesized to further examine their potential as two-photon singlet oxygen sensitizers.

Outlines of the synthetic steps used to prepare the tripodal molecules **1_T(x)** and the linear molecules **3_T(x)** are given in Schemes 4−6.

The tripodal compounds were synthesized by two different routes. In both cases, the key starting material was tris(4-iodophenyl)amine **6**, which was selectively obtained in high yield from triphenylamine according to a previously reported procedure.[36]

In the first route, **6** was coupled with arylethynes in Sonogashira couplings[37] (Scheme 4). The cyano arylethyne **5** was obtained from 4-bromobenzonitrile by a Sonogashira coupling with trimethylsilylacetylene followed by removal of the TMS group using tetrabutylammonium fluoride (TBAF). Subsequent use of **5** in the coupling with **6** gave **1_T(CN)** in excellent yield. Reduction of the three cyano groups in **1_T(CN)** using diisobutylaluminum hydride (DIBAL) yielded the trialdehyde **1_T(CHO)** in a moderate yield of 43%. The synthesis of the arylethyne used to prepare the bromoderivative **1_T(Br)** is associated with a selectivity problem. Specifically, in the synthesis of **7** from 4-bromo-1-iodobenzene, both bromo and iodo derivatives can undergo Sonogashira coupling with acetylenes. The selectivity problem is resolved by application of ethynylzinc bromide in a Negishi coupling,[38,39] which shows better selectivity for iodine compared to bromine. The selectivity problem is

TABLE 1. Relative Two-Photon Absorption Cross Sections Calculated Using Response Theory

molecule	two-photon cross sections[a] (transition energy, irreducible representation)[b]			point group[b]
1_T(H)	$\mathbf{1.67 \times 10^{4}}$ **(4.50, A(E))**[c]	4.62×10^{3} (4.87, A)	1.29×10^{3} (5.47, A)	C_1 (C_3)
1_T(CN)	8.20×10^{4} (4.35, A(E))[c]	$\mathbf{9.20 \times 10^{4}}$ **(4.67, A)**	1.26×10^{3} (5.50, A)	C_1 (C_3)
1_T(F)	$\mathbf{1.27 \times 10^{4}}$ **(4.50, A(E))**[c]	2.54×10^{3} (4.87, A)	8.66×10^{2} (5.47, A)	C_1 (C_3)
1_T(F_5)	$\mathbf{6.61 \times 10^{4}}$ **(4.45, A(E))**[c]	6.10×10^{4} (4.84, A)	1.64×10^{2} (5.53, A)	C_1 (C_3)
1_T(CHO)	9.82×10^{4} (4.30, A(E))[c]	5.49×10^{0} (4.61, A)	$\mathbf{1.24 \times 10^{5}}$ **(4.63, A)**	C_1 (C_3)
1_T(CO_2H)	1.03×10^{5} (4.35, A(E))[c]	$\mathbf{1.27 \times 10^{5}}$ **(4.68, A)**	2.11×10^{2} (5.46, A)	C_1 (C_3)
1_T(HPy^+)	8.27×10^{5} (3.90, A(E))[c]	$\mathbf{1.44 \times 10^{6}}$ **(4.30, A)**	9.05×10^{2} (4.84, A)	C_1 (C_3)
1_T(MPy^+)	8.43×10^{5} (3.91, A(E))[c]	$\mathbf{1.48 \times 10^{6}}$ **(4.31, A)**	7.19×10^{0} (4.93, A)	C_1 (C_3)
1_D(H)	$\mathbf{2.66 \times 10^{4}}$ **(4.15, A(E))**[c]	1.28×10^{4} (4.55, A)	1.86×10^{3} (5.28, A)	C_1 (C_3)
1_D(CN)	1.10×10^{5} (4.01, A(E))[c]	$\mathbf{1.26 \times 10^{5}}$ **(4.39, A)**	1.01×10^{3} (5.31, A)	C_1 (C_3)
2_T(H)	3.23×10^{3} (4.51, A)	$\mathbf{8.97 \times 10^{3}}$ **(4.80, A)**		C_1
2_T(CN)	2.04×10^{4} (4.35, A)	$\mathbf{9.61 \times 10^{4}}$ **(4.60, A)**		C_1
2_T(CHO)	2.59×10^{4} (4.33, A)	$\mathbf{1.16 \times 10^{5}}$ **(4.58, A)**		C_1
2_T(CO_2H)	2.46×10^{4} (4.37, A)	$\mathbf{1.14 \times 10^{5}}$ **(4.62, A)**		C_1
2_T(F)	2.33×10^{3} (4.54, A)	$\mathbf{5.69 \times 10^{3}}$ **(4.83, A)**		C_1
2_D(H)	5.15×10^{3} (4.18, A)	$\mathbf{1.16 \times 10^{4}}$ **(4.47, A)**		C_1
2_D(CN)	3.10×10^{4} (4.02, A)	$\mathbf{9.40 \times 10^{4}}$ **(4.31, A)**		C_1
3_T(H)	$\mathbf{1.45 \times 10^{5}}$ **(4.90, $\mathbf{A_g}$)**	4.73×10^{3} (5.50, A_g)		C_i
3_T(CN)	$\mathbf{1.27 \times 10^{6}}$ **(4.75, $\mathbf{A_g}$)**	1.26×10^{4} (5.51, A_g)		C_i
3_T(CHO)	1.01×10^{1} (4.42, A_g)	$\mathbf{6.20 \times 10^{5}}$ **(4.81, $\mathbf{A_g}$)**		C_i
3_T(CO_2H)	$\mathbf{4.56 \times 10^{5}}$ **(4.85, $\mathbf{A_g}$)**	7.34×10^{3} (5.51, A_g)		C_i
3_T(F)	$\mathbf{3.50 \times 10^{5}}$ **(4.87, $\mathbf{A_g}$)**	5.84×10^{3} (5.50, A_g)		C_i
3_T(F_2)	$\mathbf{6.49 \times 10^{5}}$ **(4.84, $\mathbf{A_g}$)**	7.08×10^{3} (5.51, A_g)		C_i
3_T(Br)[d]	$\mathbf{4.40 \times 10^{5}}$ **(5.02, $\mathbf{A_g}$)**	4.65×10^{3} (5.78, A_g)		C_i
3_D(H)	$\mathbf{1.38 \times 10^{5}}$ **(4.67, $\mathbf{A_g}$)**	1.92×10^{4} (5.40, A_g)		C_i
3_D(CN)	$\mathbf{1.21 \times 10^{6}}$ **(4.52, $\mathbf{A_g}$)**	8.23×10^{4} (5.40, A_g)		C_i
3_D(CHO)	7.81×10^{0} (4.49, A_g)	$\mathbf{5.49 \times 10^{5}}$ **(4.56, $\mathbf{A_g}$)**		C_i
3_D(F_2)	$\mathbf{6.94 \times 10^{5}}$ **(4.65, $\mathbf{A_g}$)**	2.85×10^{4} (5.41, A_g)		C_i
3_D(Br)[d]	$\mathbf{5.31 \times 10^{5}}$ **(4.76, $\mathbf{A_g}$)**	2.47×10^{4} (5.68, A_g)		C_i

[a] In atomic units. Data shown correspond to 30δ (see eq 1). For a given molecule, the transition with the largest cross section is shown in boldface type. [b] Transition energies in eV. As explained in the section on computational methods, the calculated transition energies are larger than those that would be experimentally observed. For each molecule, we identify the point group used and the corresponding irreducible representation to which the given transition transforms. [c] These entries reflect transitions to a doubly degenerate excited state. The cross sections shown are the sum of the individual cross sections to the respective excited states. In the point group C_3, these transitions transform according to the irreducible representation E. In DALTON, the molecules are examined using the point group C_1 and the separate transitions transform according to the irreducible representation A. [d] The 3-21G basis set was used.

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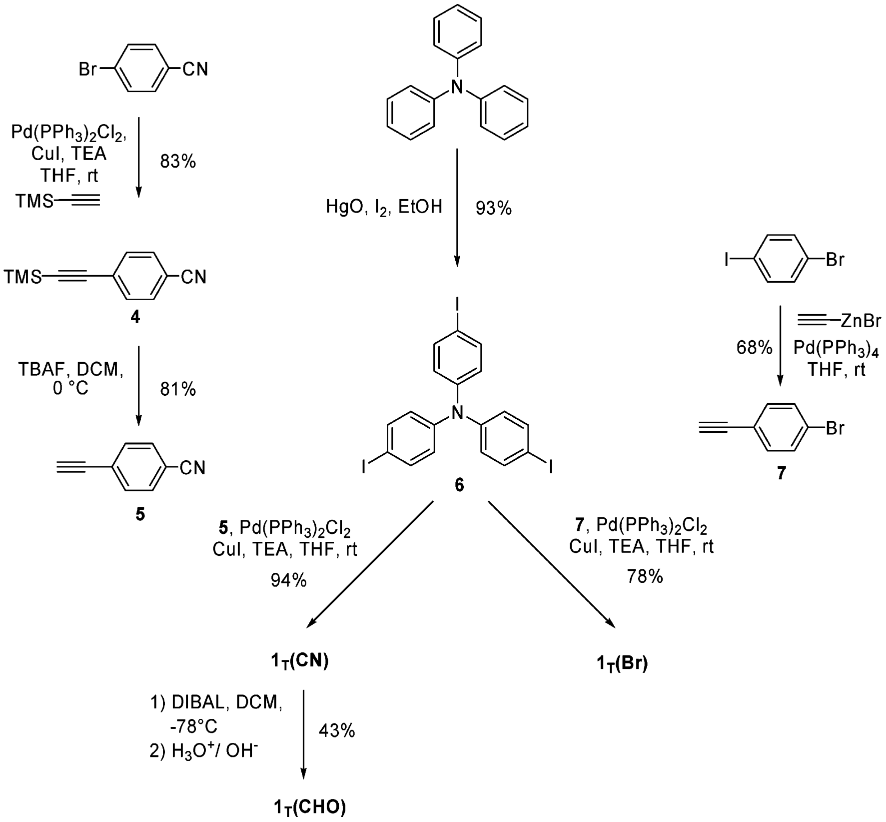
SCHEME 4



not observed in the reaction between **6** and **7**, and the Sonogashira coupling gives $\mathbf{1_T(Br)}$ in 78% yield.

In the second route, the tripodal sensitizers were synthesized via intermediate **9** (Scheme 5). This approach was prompted by the fact that attempts to use the method outlined in Scheme 4 to couple trimethylsilylacetylene with electron deficient aromatic iodo compounds, in particular the iodofluoro derivative, gave poor results. On the other hand, coupling of the iodoaryl compounds with **9** gave much better yields, even though three iodo-substituted compounds had to be coupled to **9**. Compound **9** was obtained in high yield by triple coupling of trimethylsilylacetylene with **6** and subsequent deprotection with TBAF. The sensitizers $\mathbf{1_T(CO_2CH_3)}$ and $\mathbf{1_T(F_5)}$ were obtained by standard Sonogashira couplings with the respective iodoaryl compounds. The coupling of **9** with 3 equiv of 4-bromopyridinium chloride was more difficult and required a different catalyst−ligand system to achieve an acceptable yield of $\mathbf{1_T(Py)}$. It is believed that a more nucleophilic palladium catalyst is obtained when using the *t*-Bu ligand, which enhances the rate of the oxidative addition of the catalyst to the bromopyridine.[40] The sensitizer $\mathbf{1_T(CO_2H)}$ was obtained by hydrolysis of the three esters in $\mathbf{1_T(CO_2CH_3)}$, and $\mathbf{1_T(MePy^+)}$ was obtained by methylation of $\mathbf{1_T(Py)}$. In the latter reaction, methylation of the central nitrogen atom is not observed because the lone pair of this nitrogen is delocalized and because the nitrogen atom is sterically hindered. For the spectroscopic measurements in water, $\mathbf{1_T(CO_2H)}$ was dissolved in an alkaline solution and, thus, the pertinent compound is $\mathbf{1_T(CO_2^-)}$.

The rodlike sensitizers $\mathbf{3_T(H)}$, $\mathbf{3_T(F_2)}$, and $\mathbf{3_T(Br)}$ were also synthesized using palladium chemistry (Scheme 6). In the first step of the synthesis, diphenylamine was connected to the aryl moiety in 4-bromo-1-iodobenzene by a palladium-catalyzed C−N coupling reaction.[41] With the selected conditions, the bifunctional aryl derivative preferably undergoes coupling by substitution of iodide to form **11**. However, the competing reaction at the bromide cannot be completely eliminated, and the diamine **12** is formed as a byproduct. A Sonogashira coupling reaction with 1,4-diethynylbenzene gives rise to $\mathbf{3_T(H)}$, albeit in a low yield. In the other pathway, **11** was functionalized with TMS-acetylene and subsequent removal of the TMS group gave **14** in a high yield. Coupling 2 equiv of **14** with 1,4-diiodo-2,3,5,6-tetrafluorobenzene gave $\mathbf{3_T(F_2)}$. To selectively obtain $\mathbf{3_T(Br)}$ from 1,4-dibromo-2,5-diiodobenzene and **14**, a Negishi-type coupling was preferred over the Sonogashira coupling since it has the highest preference for iodine. The zinc reagent was made by deprotonation of the electron rich ethynyl moiety in **14** with LDA and subsequent transmetalation with $ZnBr_2$. Cross-coupling with the diiodoaryl derivative gave $\mathbf{3_T(Br)}$ with high chemoselectivity in a yield of 80%.

Measurements. In assessing the potential of our molecules to act as two-photon singlet oxygen sensitizers, several issues were considered, as outlined below.

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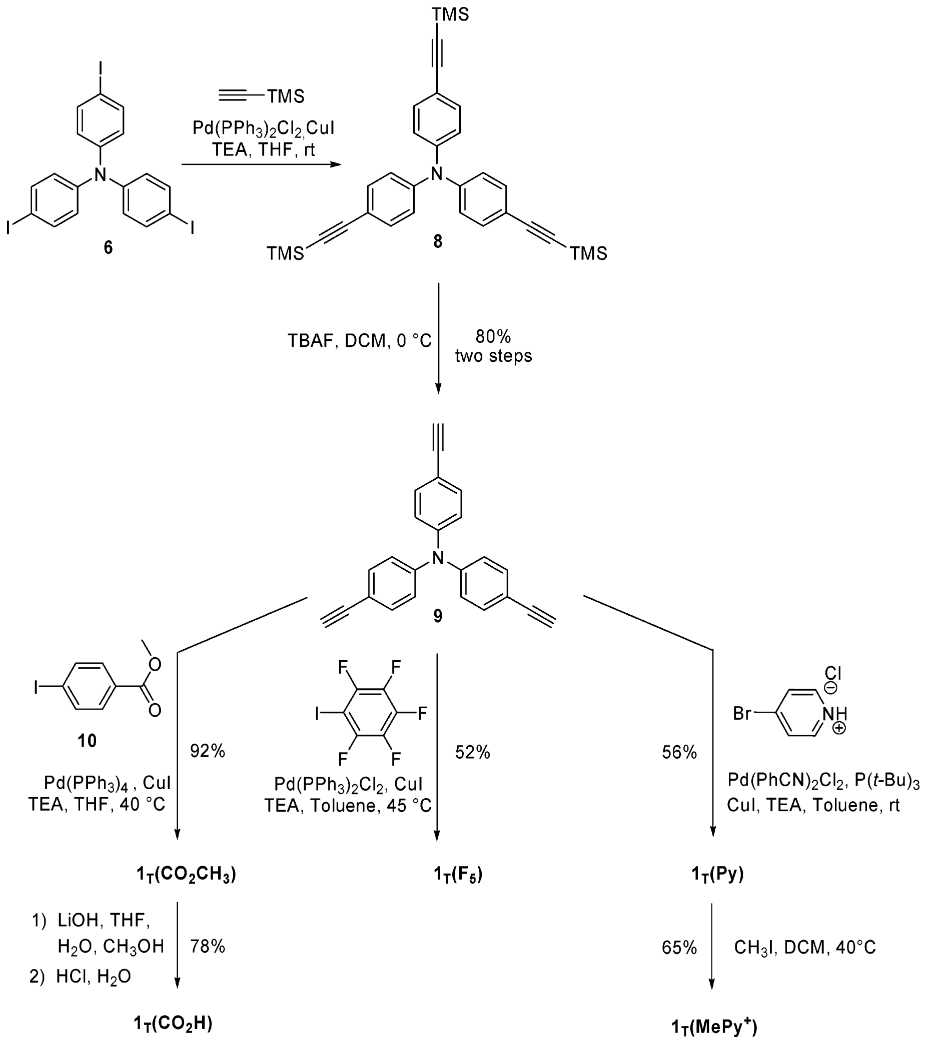
SCHEME 5



A. Singlet Oxygen Quantum Yields. The singlet oxygen quantum yield quantifies the efficiency of singlet oxygen production by the excited-state sensitizer. When using this number in the present context, we assume that the quantum yield is independent of the method by which the excited state was produced. Specifically, despite the fact that the sensitizer excited state initially produced upon two-photon irradiation may be different from that produced upon one-photon irradiation, it is reasonable to assume that rapid relaxation within the singlet state manifold will yield the same state, S_1, from which all subsequent photophysics derives (i.e., Kasha's rule[42] is followed). Thus, singlet oxygen quantum yields obtained in a one-photon experiment should be valid in the context of a two-photon discussion.

Of the tripodal phenylene−ethynylene-based chromophores, $\mathbf{1_T(x)}$, five are soluble in toluene. In this solvent, these molecules have a modest singlet oxygen yield, ranging from 0.15 to 0.24 (Table 2). On the other hand, the water-soluble tripodal chromophores with charged substituents do not produce singlet oxygen in a measurable yield (Table 2). In these latter cases, where solvent-stabilized sensitizer-oxygen charge-transfer states are likely to be readily accessible, charge-transfer-mediated deactivation of the sensitizer excited state most likely competes with the energy transfer process that results in singlet oxygen formation. This is an established phenomenon and can be quite pronounced in polar solvents.[10,43−45]

In the rodlike chromophores $\mathbf{3_T(x)}$ and $\mathbf{3_D(x)}$, the presence of the "heavy-atom" bromine on the central aromatic ring clearly has an advantageous effect on the singlet oxygen yield. In this case, the data reflect a heavy-atom-mediated increase in the extent of spin−orbit coupling that, in turn, results in a greater yield of the sensitizer triplet state which is the immediate precursor to singlet oxygen.

B. Stability. There are several ways one can quantify the relative photostability of molecules used as singlet oxygen sensitizers.

On one hand, one could directly irradiate the molecules over discrete periods of time and monitor the extent to which changes in the molecule occur (e.g., via absorption

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SCHEME 6

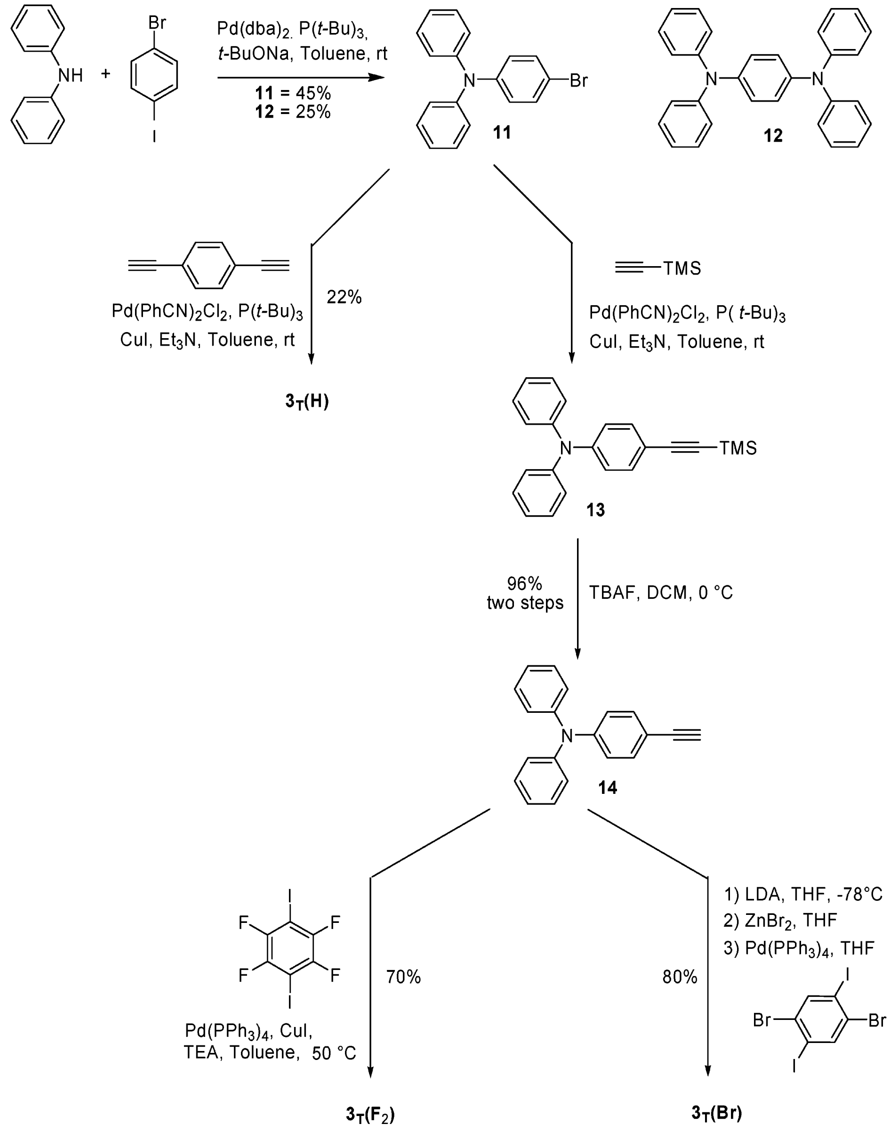

TABLE 2. Singlet-Oxygen Quantum Yields, ϕ_Δ, and One-Photon Absorption Maxima, λ_{max}(1P), for the Sensitizers Studied

molecule	λ_{max}(1P)[a] (nm)	ϕ_Δ(toluene)[b]	ϕ_Δ(water)[b]
1_T(CN)	393	0.18	
1_T(CHO)	401	0.22	
1_T(CO_2CH_3)	390	0.15	
1_T(Br)	375	0.24	
1_T(F_5)	382	0.19	
1_T(CO_2^-)	375		0
1_T(MPy^+)	448		0
3_T(H)	383	0.09	
3_T(Br)	404	0.49	
3_T(F_2)	418	0.09	
3_D(H)	411	0.08	
3_D(Br)	427	0.46	
3_D(F_2)	430	0.09	

[a] Recorded in toluene, except for 1_T(CO_2^-) and 1_T(MPy^+) which were recorded in water. [b] Recorded in air-saturated solvents. Data in water were recorded using perinaphthenone sulfonic acid as the standard ($\phi_\Delta = 1.0$),[46,47] whereas data in toluene were recorded using acridine as the standard ($\phi_\Delta = 0.83$).[48] Errors are ±10%.

spectroscopy). However, this approach has the distinct disadvantage that one must continually correct for changes in the extent to which light is absorbed over the course of the reaction.

Of course, in our case, we are particularly interested in the relative reactivity of these molecules with singlet oxygen itself. As such, we opted to use an independent sensitizer to generate singlet oxygen in the presence of the molecules whose reactivity we wished to study. We have outlined the advantages of this approach in a study of the reactivity of phenylene vinylenes.[6] For the present case, the independent sensitizer of choice is the fullerene C_{60}. It is particularly important to note that (1) upon irradiation, C_{60} generates singlet oxygen in high yield,[49] (2) C_{60} can be irradiated at wavelengths where the molecules being degraded do not absorb, (3) the extent of degradation can be followed using absorption spec-

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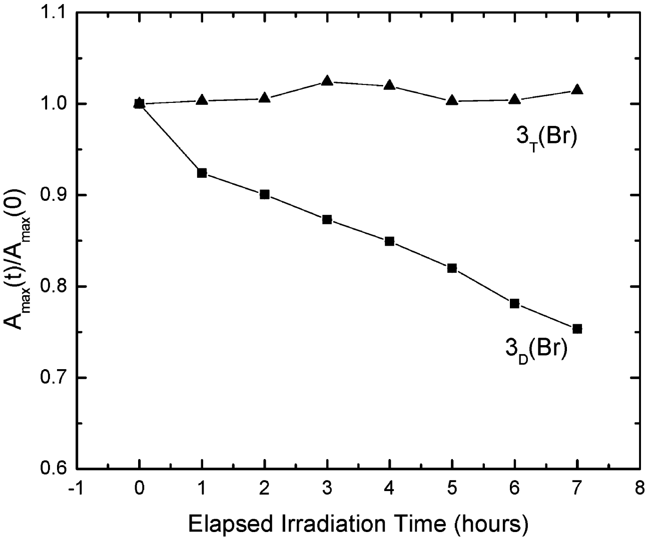

FIGURE 1. Data illustrating the relative reactivities of 3_T(Br) and 3_D(Br) to singlet oxygen. The latter was generated upon selective irradiation of an independent sensitizer, C_{60}, added to the solution. In the present experiment, the extent of degradation was quantified by monitoring substrate disappearance using absorption spectroscopy (3_T(Br) λ_{max} at 420 nm and 3_D(Br) λ_{max} at 440 nm; see Figure 2). The absorbance at time = t divided by the absorbance at time = 0 was then plotted as a function of the elapsed time of C_{60} irradiation. The experiment was performed in toluene.

troscopy at a wavelength where C_{60} does not have an appreciable absorbance, (4) the products of the degradation reactions all absorb light at wavelengths that are blue-shifted relative to the wavelength at which C_{60} is irradiated and at which the remaining unreacted substrate is monitored, and (5) C_{60} is stable upon prolonged irradiation.

In Figure 1, we show the results of a study in which the relative reactivities of **3_T(Br)** and **3_D(Br)** to singlet oxygen were compared. The data clearly show that the molecule containing alkyne moieties is less reactive than the corresponding alkene-containing molecule. This observation is also consistent with data obtained on phenylene vinylenes in which the alkenyl residue is identified as the functional group that initially reacts with singlet oxygen.[6,50]

C. One-Photon Absorption Spectra. In the development of singlet oxygen sensitizers, the absorption spectrum of a given molecule is a property that has significant influence on where and when the molecule can be used.

As illustrated in Figure 2 and Table 2, we find that, for a given chromophore, replacement of alkene moieties with alkyne moieties results in a blue shift in the one-photon absorption spectrum. This phenomenon is consistent with data recorded from other systems (e.g., 1,2-diphenylacetylene vs stilbene).[51]

The femtosecond laser system we currently use to irradiate molecules in our time-resolved two-photon singlet oxygen experiments can only be tuned over the limited wavelength range of ~765−850 nm (this range is a characteristic of an amplified laser that operates at a 1 kHz pulse repetition rate to accommodate a singlet oxygen lifetime in the microsecond domain).[10] Thus, a desirable two-photon sensitizer (1) will not have an allowed one-photon transition in this wavelength range but (2) will have allowed one-photon transitions in the range ~450−550 nm (i.e., we want λ_{max}(1P) > (765−850 nm)/2). The latter criterion reflects the fact that, at least for centrosymmetric molecules, states accessible via two-photon excitation will generally be slightly higher in energy than states accessible via one-photon excitation.[12,52] On the basis of these points, the data in Figure 2 indicate that, if anything, our rodlike chromophores may have transition energies that are somewhat higher than ideally desired (i.e., the S_1 and S_2 states are too high in energy and the corresponding transitions from S_0 are shifted too far to the blue).

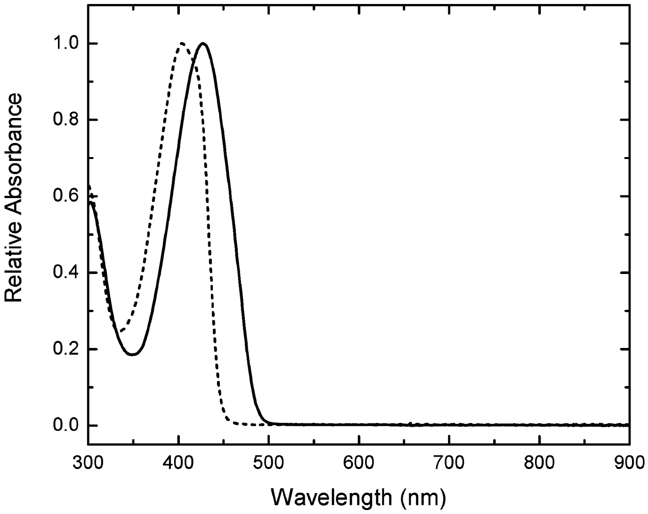

FIGURE 2. One-photon absorption spectra of 3_D(Br), solid line, and 3_T(Br), dashed line, in toluene.

D. Relative Two-Photon Absorption Spectra and Cross Sections. Of course, in the present context, the molecules used as singlet oxygen sensitizers must also have an appreciable probability for two-photon absorption over the specified wavelength range of ~765−850 nm. To quantify this particular property of a given sensitizer, we used an approach that has been described in detail elsewhere.[8−10] Briefly, for a given molecule under study and for irradiation at a given wavelength, we compared the intensity of the two-photon photosensitized singlet oxygen phosphorescence signal to the intensity of the singlet oxygen signal obtained upon two-photon irradiation of a molecule chosen as a standard. With this approach, it is only necessary to account for the respective singlet oxygen quantum yields in order to obtain relative values of the absorption cross section. For a given molecule, accurate values of the singlet oxygen quantum yield are readily obtained in an independent experiment.

For the present study, the molecule chosen as the two-photon standard was **3_D(CN)**. The two-photon absorption profile we have independently obtained for **3_D(CN)** in toluene is shown in Figure 3.[10] Although values reported for the absolute absorption cross section of **3_D(CN)** at its

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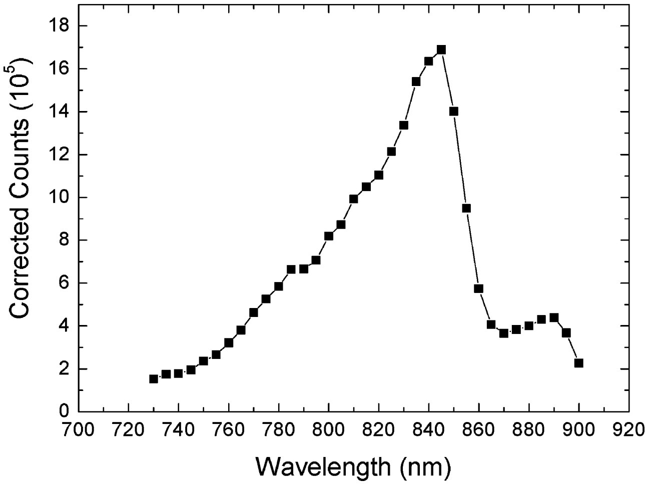

FIGURE 3. Two-photon excitation spectrum of 3_D(CN), the molecule used as a standard for the wavelength-dependent two-photon cross section measurements. The data were recorded using the fluorescence of 3_D(CN) as the probe with a 80 MHz fs laser system that has a much wider tuning range than that used for our time-resolved singlet oxygen experiments.[10]

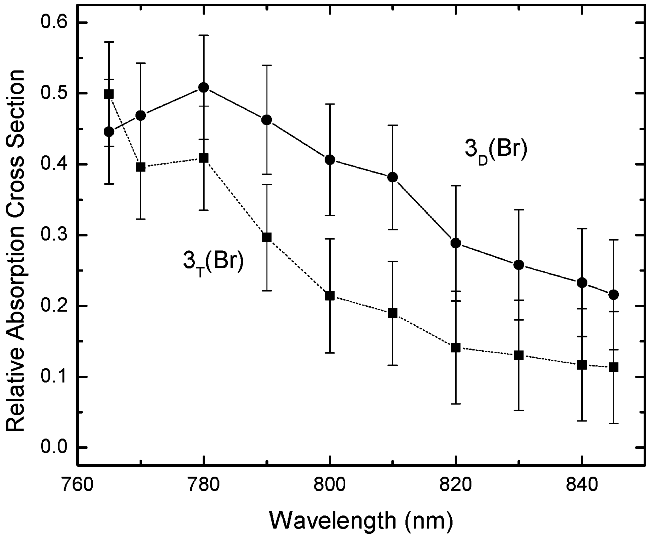

FIGURE 4. Plot of the relative absorption cross section against the irradiation wavelength for the two-photon excitation of 3_D(Br) and 3_T(Br) in toluene. The data were obtained in singlet oxygen phosphorescence experiments in which 3_D(CN) was used as the two-photon absorption standard.

band maximum cover a large range,[22,53,54] the data indicate that the molecule has a comparatively large two-photon cross section at ~840 nm (e.g., (1890 ± 280) × 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$).[53]

In Figure 4, we show two-photon absorption spectra obtained for **3_D(Br)** and **3_T(Br)**. Several points deserve comment. First, the data clearly indicate that, over the wavelength range studied, the alkyne-based sensitizer, **3_T(Br)**, does not absorb light as well as the alkene-based sensitizer, **3_D(Br)**. The data obtained, however, appear to indicate that the difference in cross section values at a given wavelength is simply a consequence of the fact that the two-photon absorption spectrum of **3_D(Br)** is red-shifted relative to the two-photon absorption spectrum of **3_T(Br)**. This interpretation is certainly consistent with the one-photon data shown in Figure 2 and the computations shown in Table 1. Second, although **3_T(Br)** and **3_D(Br)** do not have absorption cross sections as large as the standard **3_D(CN)** over this wavelength range, the cross sections at ~780 nm are sufficiently large to facilitate the use of these molecules in a range of applications.

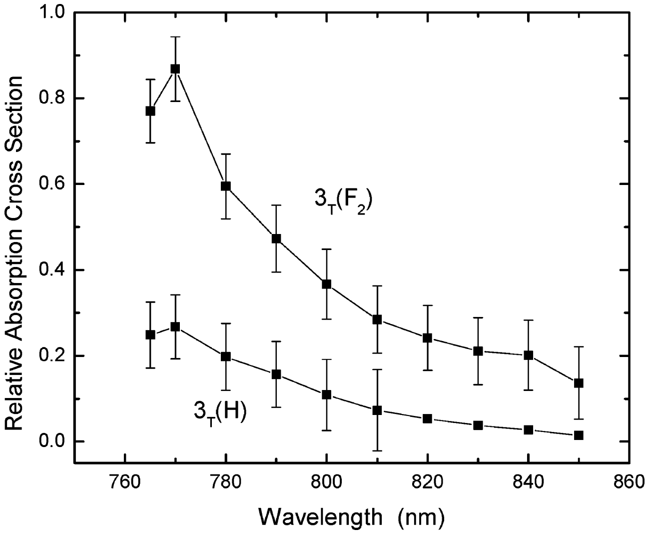

FIGURE 5. Plot of the relative absorption cross section against the irradiation wavelength for the two-photon excitation of $3_T(F_2)$ and 3_T(H) in toluene. The data were obtained in singlet oxygen phosphorescence experiments in which 3_D(CN) was used as the two-photon absorption standard.

Of the alkyne-based sensitizers that produce singlet oxygen in measurable yield, we ascertained that **$3_T(F_2)$** has the largest two-photon absorption cross section in the wavelength range 765−850 nm (Figure 5). In Figure 6 we show two-photon absorption spectra obtained for the tri-podal alkyne-containing sensitizers, **1_T(x)**. In this case, we find that the largest absorption cross section obtained (i.e., that for **$1_T(CO_2CH_3)$** at ~770 nm) is a factor of ~2.5 times smaller than the largest cross section obtained for the rod-shaped molecules (i.e., that for **$3_T(F_2)$** at ~770 nm).

For all of the molecules examined, the relative differences in the maximum two-photon absorption cross section experimentally measured are consistent with the differences expected based on our computations (Table 1).

It is prudent at this point to comment on the apparent peak observed at 770 nm in the two-photon absorption spectra shown in Figures 5 and 6. Even though the data were recorded in a relative experiment against a standard, it is important to note that, at 765 nm, the fs system used to irradiate the sample is operating at its limit in which the output power, pulse temporal profile, and spectral content have the largest uncertainty. With respect to the latter point, it is also important to note that, with fs lasers, the spectral bandwidth at a given irradiation "wavelength" is quite broad (~15 nm). As a consequence, any subtle substituent−dependent changes

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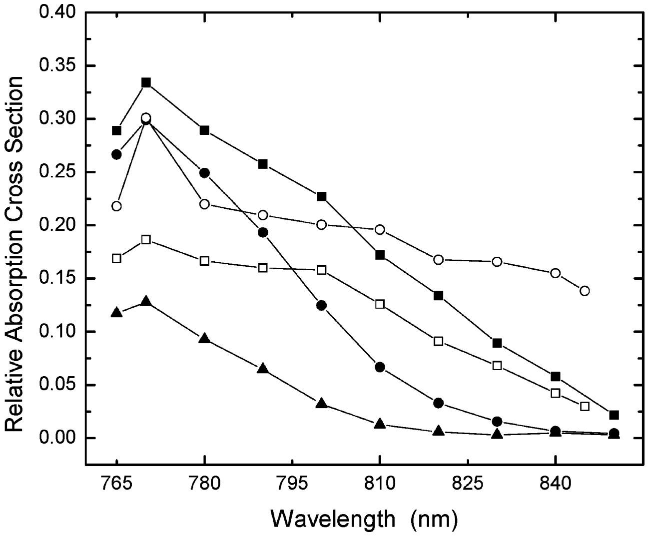

FIGURE 6. Plot of the relative absorption cross section against the irradiation wavelength for the two-photon excitation of five tri-podal molecules in toluene: $1_T(CO_2CH_3)$, ■; $1_T(F_5)$, ●; $1_T(CHO)$, ○; $1_T(CN)$, □; $1_T(Br)$, ▲. The data were obtained in singlet oxygen phosphorescence experiments in which $3_D(CN)$ was used as the two-photon absorption standard (error ~ ±10−15%).

in the actual position of the absorption band maximum may not be resolved with our available spectral resolution.

Conclusions

Not only are singlet oxygen photosensitizers that contain a triple bond as an integral part of the chromophore viable, but they also have one distinctive and attractive feature that sets them apart from the corresponding alkene-containing sensitizer; the alkynyl moiety is significantly less susceptible to reaction with singlet oxygen. Specifically, alkyne-containing sensitizers retain essentially all of the desirable linear and nonlinear optical properties of the corresponding alkene-containing molecule but can be used over significantly longer periods of irradiation. The latter can have significant consequences in singlet oxygen imaging experiments where prolonged periods of data acquisition may be required.

Experimental Section

Computational Methods. Features of our ab initio computational approach have been described previously.[9] Briefly, calculations were performed with the DALTON program package,[55] using response theory to obtain the two-photon absorption cross sections. For this application, the principal attribute of response theory is the ability to obtain the two-photon cross section in one calculation in which the virtual state is effectively described as a linear combination of all states of the molecule.[56] Thus, we explicitly avoid the limitations of a traditional sum-over-states calculation[57−59] in which the accuracy of the result can be compromised if one, or more, key states of the molecule are neglected.

In our approach, the matrix elements for a two-photon electric dipole transition, $S_{\alpha,\beta}$, were calculated through a residue of the quadratic response function.[56] The two-photon cross section for linearly polarized light, δ, was then expressed in terms of these matrix elements, summed over the molecular axes (eq 1, where $\alpha = x, y, z$ and $\beta = x, y, z$).[58,60]

$$\delta = \frac{1}{30}\sum_{\alpha,\beta}(2S_{\alpha,\alpha}S^*_{\beta,\beta} + 4S_{\alpha,\beta}S^*_{\beta,\alpha}) \tag{1}$$

Unless stated otherwise, the response calculations were carried out using the 6-31G* basis set.

Prior to using the DALTON package for the response calculations, the geometries of the respective molecules were optimized using a number of approaches available in the Gaussian 98 program.[61] We have demonstrated that, for a given molecule, calculated two-photon transition energies and absorption cross sections can depend significantly on the molecular geometry used.[9] This is indeed to be expected, particularly when the geometric variable influences the extent of conjugation in the system. For these reasons, when performing the geometry optimizations, we not only tried to be thorough in the search for "the" global minimum, but we also tried to be consistent in an attempt to ensure that relative changes in the respective cross sections would be accurate.

The absorption cross section obtained from the response theory computation is in atomic units. To compare the latter with experimental data, it is necessary to convert to a number with the units of cm^4 s $photon^{-1}molecule^{-1}$. Among other things, this transformation involves multiplication by a band shape function that can vary from one molecule to the next.[9,35,52,62] For our present application, in which we want only to focus on relative changes in the magnitude of the absorption cross section, we have opted to avoid introducing this extra source of uncertainty.

It is likewise important to recognize that, due to the size of the systems involved, the calculations were performed on the uncorrelated Hartree−Fock level. Moreover, the effect of solvent has not been included. As a consequence, the calculated transition energies are generally larger than those that would be experimentally observed from solution phase systems. Although this is a general problem common to such computations,[33,34] the calculated differences between transition energies should be reasonably accurate.

Sensitizer Synthesis. Standard Schlenk techniques were employed using argon as the inert atmosphere for all manipulations of air- or moisture-sensitive compounds. Unless otherwise stated, yields refer to chromatographically isolated and

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spectroscopically pure materials. Commercially available starting materials were used as received without further purification. Flash chromatography was performed using Merck silica gel 60 (230−400 mesh). THF was freshly distilled over sodium wire and DCM was freshly distilled over CaH_2. Toluene, triethylamine and diisopropylamine were distilled over CaH_2 and stored under Argon over molecular sieves. $ZnBr_2$ was flame-dried at <1 mmHg shortly before use. Sodium *tert*-butoxide was stored in a glovebox and small portions were removed in glass vials, stored in the air in desiccators, weighed in the air, and consumed within a week. 1,3-Diethynylbenzene,[63,64] tris-(4-iodophenyl)amine (**6**),[36] and 4-iodobenzoic acid methyl ester (**10**)[65] were synthesized according to literature procedures.

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 400, 100, and 376 MHz, respectively. For the fluorinated compounds **$1_T(F_5)$**, **$3_T(F_2)$**, and **$3_D(F_2)$**, the ^{13}C NMR signals from the atoms on and near the fluorinated phenyl ring were not discernible from the background noise. Specifically, when using traditional ^{13}C NMR techniques that lack special broadband C−F decoupling schemes, the pertinent carbon signals are split into a number of low intensity peaks due to the comparatively large carbon−fluorine coupling constants.[66]

4-Trimethylsilanylethynylbenzonitrile (4). A flame-dried Schlenk flask was charged with 4-bromobenzonitrile (200 mg, 1.105 mmol), $Pd(PPh_3)_2Cl_2$ (40 mg, 0.055 mmol), and CuI (26 mg, 0.11 mmol). After three successive vacuum/argon cycles, THF (4 mL), trimethylsilylacetylene (0.321 mL, 2.21 mmol), and triethylamine (1 mL) were introduced via syringe. Once triethylamine was added, the reaction mixture turned black. The mixture was stirred at rt for 15 h, diluted with Et_2O, washed with aqueous NH_4Cl and then with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (pentane/Et_2O = 95/5, v/v) gave 168 mg (83%) of **4**. Spectroscopic data were consistent with those reported previously for this compound.[67]

4-Ethynylbenzonitrile (5). In a one-neck round-bottom flask, **4** (223 mg, 1.12 mmol) was dissolved in DCM (10 mL). The flask was cooled to 0 °C and a 1 M solution of tetrabutylammoniumfluoride in THF (1.34 mL, 1.34 mmol) was added via syringe. The reaction mixture was stirred for 2 h at 0 °C, washed twice with water, dried over $MgSO_4$, filtered and concentrated. Chromatography on silica gel (pentane/Et_2O = 95/5, v/v) gave 115 mg (81%) of **5**. Spectroscopic data were consistent with those reported previously for this compound.[67]

Tris-4,4′,4″-(4-cyanophenylethynyl)triphenylamine (1_T(CN)). A flame-dried Schlenk flask was charged with 4-ethynylbenzonitrile **5** (115 mg, 0.907 mmol), tris(4-iodophenyl)amine (146 mg, 0.234 mmol), $Pd(PPh_3)_2Cl_2$ (25 mg, 0.035 mmol), and CuI (13 mg, 0.070 mmol). After three successive vacuum/argon cycles, THF (6 mL) and triethylamine (1.5 mL) were introduced via syringe. Once triethylamine was added, the reaction mixture turned black. The mixture was stirred at room temperature for 15 h and concentrated in vacuo, and the crude product was taken up in DCM, washed with aqueous NH_4Cl and then with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (neat DCM) gave 136 mg (94%) of **1_T(CN)**: mp 234−236 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.10 (d, 6H, J = 8.6 Hz), 7.46 (d, 6H, J = 8.6 Hz), 7.59 (d, 6H, J = 8.4 Hz), (d, 6H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 87.9, 93.6, 111.3, 117.1, 118.5, 124.1, 128.2, 131.9, 132.0, 133.1, 147.0; HRMS *m/z* calcd for $C_{45}H_{24}N_4$ 620.2001, found 620.2010.

Tris-4,4′,4″-(4-formylphenylethynyl)triphenylamine (1_T(CHO)). In a flame-dried Schlenk flask, **1_T(CN)** (200 mg, 0.32 mmol) was dissolved in DCM (6 mL) and cooled to −78 °C. A 1.5 M solution of DIBAL in toluene (1.16 mL, 1.74 mmol) was added dropwise via syringe. The mixture was warmed to rt over 2 h under constant stirring. An excess of 5 M HCl (6 mL) was slowly added, and stirring was continued for 1 h. Aqueous NaOH was used to render the solution alkaline, and the organic phase was separated, washed once with water, dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (neat DCM) gave 84 mg (43%) of **1_T(CHO)**: mp 210−211 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.11 (d, 6H, J = 8.5 Hz), 7.48, (d, 6H, J = 8.5 Hz), 7.66 (d, 6H, J = 8.1 Hz), 7.87 (d, 6H, J = 8.1 Hz), 10.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 88.7, 93.3, 117.3, 124.1, 129.6, 131.9, 133.1, 135.2, 147.0, 191.4; HRMS *m/z* calcd for $C_{45}H_{27}NO_3$ 629.7008, found 629.2016.

4-Bromoethynylbenzene (7). A flame-dried Schlenk flask was charged with a solution of ethynylmagnesium bromide (2.4 mL of a 0.5 M solution in THF, 1.22 mmol). A solution of anhydrous $ZnBr_2$ (293 mg, 1.22 mmol) in THF (3 mL) was added via cannula at 0 °C. The mixture was stirred for 30 min and added, via cannula, to a solution of 4-bromoiodobenzene (345 mg, 1.22 mmol) and $Pd(PPh_3)_4$ (75 mg, 0.065 mmol) in THF (3 mL). The reaction mixture was stirred at rt for 15 h, diluted with Et_2O (7 mL), washed once with aqueous NH_4Cl, once with aqueous $NaHCO_3$, and once with brine, dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (pentane/DCM = 90/10, v/v) gave 150 mg (68%) of **7**. Spectroscopic data were consistent with those reported previously for this compound.[68,69]

Tris-4,4′,4″-(4-bromophenylethynyl)triphenylamine (1_T(Br)). A flame-dried Schlenk flask was charged with tris(4-iodophenyl)amine (156 mg, 0.25 mmol), $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol), and CuI (4.8 mg, 0.025 mmol). After three successive vacuum/argon cycles, THF (6 mL), 4-bromoethynylbenzene **7** (150 mg, 0.8 mmol), and triethylamine (2 mL) were introduced via syringe. Once triethylamine was added, the reaction mixture turned black. The mixture was stirred at rt for 15 h, diluted with DCM, and forced through a short pad of silica. The solvent was removed in vacuo and the crude product was absorbed onto silica. Chromatography on silica gel with gradient elution (pentane/DCM from 95/5 to 80/20, v/v) gave 152 mg (78%) of **1_T(Br)**: mp 238−240 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.07 (d, 6H, J = 8.6 Hz), 7.37 (d, 6H, J = 8.5 Hz), 7.42 (d, 6H, J = 8.6 Hz), 7.48 (d, 6H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 88.3, 90.3, 117.6, 122.2, 122.3, 124.0, 131.6, 132.8, 132.9, 146.7; HRMS *m/z* calcd for $C_{42}H_{24}Br_3N$ 778.9459, found 778.9479.

Tris(4-ethynylphenyl)amine (9). A flame-dried Schlenk flask was charged with tris(4-iodophenyl)amine (623 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), and CuI (19 mg, 0.1 mmol). After three successive vacuum/argon cycles, THF (8 mL), trimethylsilylacetylene (0.57 mL, 4.0 mmol), and triethylamine (2 mL) were introduced via syringe. Once triethylamine was added the reaction mixture turned black. The mixture was stirred at rt for 15 h, diluted with Et_2O, and forced through a short pad of silica. The solvent was removed in vacuo, and the crude **8** was placed in a round-bottom flask and dissolved in DCM (10 mL). The flask was cooled to 0 °C, and tetrabutylammonium fluoride (3.0 mL of a 1 M solution in THF, 3.0 mmol) was added via syringe. The reaction mixture was stirred for 2 h at 0 °C and successively absorbed onto silica. Chromatography on silica gel (pentane/DCM = 90/10, v/v) gave 252 mg (80%) of **9**. Spectroscopic data were consistent with those reported previously for this compound.[70]

Tris-4,4′,4″-(pentafluorophenylethynyl)triphenylamine ($1_T(F_5)$). A flame-dried Schlenk flask was charged with tris(4-ethynylphenyl)amine **9** (63.5 mg, 0.2 mmol), iodopen-

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tafluorobenzene (0.093 mL, 0.7 mmol), Pd(PPh$_3$)$_4$ (23.1 mg, 0.02 mmol), and CuI (7.6 mg, 0.04 mmol). After three successive vacuum/argon cycles, toluene (4 mL) and triethylamine (1 mL) were added via syringe. The reaction mixture was stirred at 45 °C for 72 h, diluted with DCM, and forced through a short pad of silica. The solvent was removed in vacuo, and the crude product was absorbed onto silica. Chromatography on silica gel with gradient elution (pentane/DCM from 90/10 to 80/20, v/v) gave 85.2 mg (52%) of **1_T(F$_5$)**: mp 225−227 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.11 (d, 6H, J = 8.7 Hz), 7.50 (d, 6H, J = 8.7 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 73.9, 102.0, 116.5, 124.1, 133.3, 137.6 (d, J = 252.3 Hz), 141.3 (d, J = 257.0 Hz), 147.0 (d, J = 252.8 Hz), 148.1; ^{19}F NMR (CDCl$_3$, 376.256 MHz) δ − 136.2 (dd, $J_{o,p}$ = 7.0 Hz, $J_{o,m}$ = 21.6 Hz), −153.3 (t, J = 20.8 Hz), −162.2 (ddd, $J_{o,o'}$ = 6.5 Hz, $J_{m,o}$ = $J_{m,p}$ = 20.5 Hz); HRMS *m/z* calcd for $C_{42}H_{12}F_{15}N$ 815.0730, found 815.0670.

Tris-4,4′,4″-(pyridine-4-ylethynyl)triphenylamine (1_T(Py)). In a flame-dried Schlenk flask, 4-bromopyridine hydrochloride (156 mg, 0.8 mmol) and triethylamine (1.5 mL) were vigorously stirred for 15 min. During this time a white precipitate formed. Thereafter, Pd(PhCN)$_2$Cl$_2$ (10.7 mg, 0.028 mmol), CuI (3.80 mg, 0.02 mmol), and tris(4-ethynylphenyl)amine **9** (63.5 mg, 0.2 mmol) were successively added. Toluene (3 mL) and P(t-Bu)$_3$ (0.14 mL of a 0.4 M solution in hexane, 0.07 mmol) were then introduced via syringe. The Schlenk flask was wrapped in aluminum foil to keep the reaction mixture in the dark. The reaction mixture was stirred at rt for 15 h and then partitioned between DCM (10 mL) and aqueous NaHCO$_3$ (10 mL). The organic phase was dried over MgSO$_4$, filtered, and concentrated. Chromatography on silica gel (EtOAc/triethylamine = 90/10, v/v) gave 62 mg (56%) of **1_T(Py)**. Spectroscopic data were consistent with those reported previously for this compound.[71]

Tris-4,4′,4″-[*N*-(4-methyl)-4-pyridinioethynyl]triphenylamine Trisiodidide (1_T(MePy$^+$)). A flame-dried Schlenk tube was charged with **1_T(Py)** (62 mg, 0.113 mmol), methyl iodide (0.5 mL, 8.0 mmol), and DCM (5 mL). The reaction mixture was stirred at 60 °C for 1 h and then at 40 °C for 12 h. The solvent was removed in vacuo and the dark red residue taken up with a mixture of MeOH (7 mL) and EtOAc (7 mL). The solvent was removed under vacuum furnishing 70 mg (64%) of **1_T(MePy$^+$)**: mp 210−215 °C dec; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.31 (s, 9H), 7.23 (d, 6H, J = 8.7 Hz), 7.72 (d, 6H, J = 8.7 Hz), 8.22 (d, 6H, J = 6.8 Hz), 8.98 (d, 6H, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 47.7, 85.6, 102.2, 115.0, 124.5, 128.6, 134.3, 138.2, 145.4, 147.7.

Tris-4,4′,4″-(4-methoxycarbonylphenylethynyl)triphenylamine (1_T(CO$_2$CH$_3$)). A flame-dried Schlenk flask was charged with **9** (63.5 mg, 0.2 mmol), **10** (202.6 mg, 0.8 mmol), Pd(PPh$_3$)$_4$ (23.1 mg, 0.02 mmol), and CuI (3.8 mg, 0.02 mmol). After three successive vacuum/argon cycles, toluene (4 mL) and triethylamine (1 mL) were added via syringe. The Schlenk flask was sealed, and the reaction mixture was stirred at 40 °C for 15 h. After being cooled to rt, the mixture was diluted with DCM and forced through a short pad of silica. The solvent was removed in vacuo, and the crude product was absorbed onto silica. Chromatography on silica gel (neat DCM) gave 133 mg (92%) of **1_T(CO$_2$CH$_3$)**: mp 210−215 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.93 (s, 9H), 7.10 (d, 6H, J = 8.5 Hz), 7.46 (d, 6H, J = 8.5 Hz), 7.57 (d, 6H, J = 8.3 Hz), 8.02 (d, 6H, J = 8.3 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 52.2, 88.7, 92.2, 117.5, 124.1, 128.0, 129.3, 129.5, 131.3, 132.9, 146.9, 166.5; HRMS *m/z* calcd for $C_{48}H_{33}NO_6$ 719.2308, found 719.2308.

Tris-4,4′,4″-(4-carboxyphenylethynyl)triphenylamine (1_T(CO$_2$H)). A round-bottom flask was charged with **1_T(CO$_2$CH$_3$)** (88 mg, 0.12 mmol) and THF (10 mL). Once a clear solution was obtained, water (1.7 mL), MeOH (1.7 mL), and LiOH (24 mg, 0.72 mmol) were added, and the solution was stirred at rt for 15 h. A 1 M HCl solution was then added dropwise to render the solution acidic. The volume was reduced under vacuo to 2 mL, and water (10 mL) was added causing the formation of green-yellow crystals. Filtration and drying under vacuum yielded 79 mg (96%) of **1_T(CO$_2$H)**: mp 259−262 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.35 (br, 3H), 7.10 (d, 6H, J = 8.3 Hz), 7.56 (d, 6H, J = 8.3 Hz), 7.65 (d, 6H, J = 8.0 Hz), 7.63 (d, 6H, J = 8.0 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 88.5, 91.9, 116.6, 124.1, 126.7, 129.5, 130.3, 131.3, 133.1, 146.5, 166.7.

(4-Bromophenyl)diphenylamine (11) and *N,N,N′,N′*-Tetraphenyl-1,4-phenylenediamine (12). A flame-dried Schlenk flask was charged with diphenylamine (677 mg, 4.0 mmol), 4-bromoiodobenzene (1132 mg, 4.0 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (41.4 mg, 0.04 mmol), and NaO-t-Bu (577 mg, 6.0 mmol). After three successive vacuum/argon cycles, toluene (6 mL) and P(t-Bu)$_3$ (0.2 mL of a 0.4 M solution in hexane, 0.08 mmol) were added via syringe. The reaction mixture was stirred at rt for 4 h and the solvent removed in vacuo. The crude product was taken up with some DCM and absorbed onto silica gel. Chromatography on silica gel with gradient elution (pentane/DCM from 95/5 to 80/20, v/v) gave 582 mg (45%) of **11** and 399 mg (25%) of **12**. Spectroscopic data for **11** and **12** were consistent with those reported previously for these compounds.[41,72,73]

Bis[4-(*N,N*-diphenylamino)phenylethynyl]benzene (3_T(H)). A flame-dried Schlenk tube was charged with **11** (324 mg, 1.0 mmol), 1,4-diethynylbenzene (57 mg, 0.45 mmol), Pd(PhCN)$_2$Cl$_2$ (10.4 mg, 0.027 mmol), and CuI (3.4 mg, 0.018 mmol). After three successive vacuum/argon cycles, toluene (6 mL), P(t-Bu)$_3$ (0.2 mL of a 0.4 M solution in hexane, 0.08 mmol) and triethylamine (1 mL) were added via syringe. The reaction mixture was stirred at rt for 48 h and the solvent removed in vacuo. The crude product was taken up in DCM, washed with aqueous NH$_4$Cl and then with aqueous NaHCO$_3$, dried over MgSO$_4$, filtered, and concentrated. Chromatography on silica gel (pentane/DCM = 70/30, v/v) gave 60 mg (22%) of **3_T(H)**: mp 196−198 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.00 (d, 4H, J = 8.6 Hz), 7.07 (t, 4H, J = 7.4 Hz), 7.12 (d, 8H, J = 8.0 Hz), 7.28 (t, 8H, J = 7.9 Hz), 7.37 (d, 4H, J = 8.6 Hz), 7.46 (s, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 88.5, 91.5, 115.7, 122.1, 123.0, 123.6, 125.5, 129.4, 131.3, 132.5, 147.1, 148.0; HRMS *m/z* calcd for $C_{46}H_{32}N_2$ 612.2565, found 612.2554.

(4-Ethynylphenyl)diphenylamine (14). A flame-dried Schlenk flask was charged with **11** (324 mg, 1.0 mmol), trimethylsilylacetylene (170 mL, 1.2 mmol), Pd(PhCN)$_2$Cl$_2$ (11.5 mg, 0.03 mmol), and CuI (3.82 mg, 0.02 mmol). After three successive vacuum/argon cycles, toluene (6 mL), P(t-Bu)$_3$ (0.2 mL of a 0.4 M solution in hexane, 0.08 mmol), and triethylamine (1 mL) were added via syringe. The reaction mixture was stirred at rt for 15 h, diluted with Et$_2$O, and forced through a short pad of silica. The solvent was removed in vacuo, and the crude product was placed in a round-bottom flask and dissolved in DCM (6 mL). The flask was cooled to 0 °C, and a 1 M tetrabutylammonium fluoride solution in THF (1.5 mL, 1.5 mmol) was added via syringe. The reaction mixture was stirred for 2 h at 0 °C and successively absorbed onto silica. Chromatography on silica gel (pentane/DCM = 93/7, v/v) gave 259 mg (96%) of **14**: mp 80−82 °C; ^{1}H and ^{13}C NMRs were consistent with those reported previously for these compounds;[72] HRMS *m/z* calcd for $C_{20}H_{15}N$ 269.1204, found 269.1212.

Bis[4-(*N,N*-diphenylamino)phenylethynyl]tetrafluorobenzene (3_T(F$_2$)). A flame-dried Schlenk flask was charged with **14** (100 mg, 0.37 mmol), 1,4-diodotetrafluorobenzene (70 mg, 0.176 mmol), Pd(PPh$_3$)$_4$ (16.3 mg, 0.08 mmol), and CuI (2.70 mg, 0.08 mmol). After three successive vacuum/argon cycles, toluene (5 mL) and triethylamine (1 mL) were

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added via syringe. The reaction mixture was stirred at 50 °C for 48 h, diluted with DCM, and forced through a short pad of silica. The solvent was removed in vacuo and the crude product was absorbed onto silica. Chromatography on silica gel with gradient elution (pentane/DCM from 90/10 to 70/30, v/v) gave 85.3 mg (70%) of **$3_T(F_2)$**: mp 258−260 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.01 (d, 4H, J = 8.3 Hz), 7.10 (t, 4H, J = 7.5 Hz), 7.13 (d, 8H, J = 8.1 Hz) 7.30 (t, 8H, J = 7.6 Hz) 7.41 (d, 4H, J = 8.3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 103.6, 113.7, 121.4, 124.02, 125.4, 129.5, 132.9, 146.8, 149.1; ^{19}F NMR ($CDCl_3$, 376.256 MHz) δ −138.4 (s, 4F); HRMS *m/z* calcd for $C_{46}H_{28}F_4N_2$ 684.2189, found 684.2136.

1,4-Bis[4-(*N,N*-diphenylamino)phenylethynyl]2,5-dibromobenzene (3_T(Br)). A flame-dried Schlenk flask was charged with *N,N*-diisopropylamine (0.141 mL, 1.0 mmol) and THF (5 mL) and cooled to 0 °C. Thereafter, *n*-BuLi (0.625 mL of 1.6 M solution in hexane, 1.0 mmol) was added via syringe dropwise. After 30 min, a THF solution of **14** (269 mg, 1.0 mmol in 2 mL) was added to the solution via cannula at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, treated with a solution of anhydrous $ZnBr_2$ (225 mg, 1.0 mmol) in THF (2 mL), and warmed gradually to 0 °C over 30 min. 1,4-Dibromo-2,5-diiodobenzene (244 mg, 0.5 mmol)[74] and Pd(PPh_3)$_4$ (58 mg, 0.05 mmol) were added to the reaction mixture at 0 °C, which was then stirred at rt for 15 h. The reaction mixture was then diluted with DCM (20 mL) and washed once with aqueous NH_4Cl and once with aqueous $NaHCO_3$. The combined aqueous phases were backwashed with 10 mL of DCM, and then the combined organics were dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel with gradient elution (pentane/DCM from 90/10 to 70/30, v/v) gave 311 mg (80%) of **3_T(Br)**: mp 267−269 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.01 (d, 4H, J = 8.8 Hz), 7.08 (t, 4H, J = 7.3 Hz), 7.12 (d, 8H, J = 8.4 Hz), 7.29 (t, 8H, J = 8.0 Hz), 7.40 (d, 4H J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 86.4, 97.2, 114.7, 121.7, 123.4, 123.9, 125.2, 126.2, 129.4, 132.7, 135.6, 146.9, 148.6; HRMS *m/z* calcd; for $C_{46}H_{30}Br_2N_2$ 768.0776, found 768.0806.

(*E,E*)-2,5-Dicyano-1,4-bis(2-(4-diphenylaminophenyl)-vinyl)benzene (**3_D(CN)**) and **(*E,E*)-2,5-dibromo-1,4-bis(2-(4-diphenylaminophenyl)vinyl)benzene** (**3_D(Br)**) were synthesized via Horner−Wadsworth−Emmons reactions in an approach that has been outlined elsewhere.[8,53]

(*E,E*)-1,4-Bis(2-(4-diphenylaminophenyl)vinyl)benzene (**3_D(H)**). [4-(Diethoxyphosphorylmethyl)benzyl]phosphonic acid diethyl ester (2.44 g, 6.45 mmol) and 4-diphenylaminobenzaldehyde (3.20 g, 11.7 mmol), both prepared using published procedures,[75,76] were dissolved in 80 mL of DMF and purged with Ar for 15 min. KO-*t*-Bu (2.61 g, 23.3 mmol) was then added, and the reaction mixture was refluxed for 30 min under Ar atmosphere. After being cooled to rt, the reaction was quenched with water. The precipitated product was filtered and dried yielding 3.46 g (87%) of **3_D(H)** as a yellow powder: mp 206−208 °C; ^{1}H NMR($CDCl_3$) 7.49 (s, 4H), 7.41 (d, 4H, J = 8.7 Hz), 7.33−7.20 (m, 10H), 7.19−6.96 (m, 18H); ^{13}C NMR($CDCl_3$) 147.6, 147.4, 136.7, 131.6, 129.3, 127.9, 127.3, 126.7, 126.6, 124.5, 123.6, 123.0. Anal. Calcd for $C_{46}H_{36}N_2$: C, 89.58; H, 5.88; N, 4.54. Found: C, 89.26; H, 5.97; N, 4.40.

(*E,E*)-2,3,5,6-Tetrafluoro-1,4-bis(2-(4-diphenylaminophenyl)vinyl)benzene ($3_D(F_2)$). [4-(Diethoxyphosphorylmethyl)-2,3,5,6-tetrafluorobenzyl]phosphonic acid diethyl ester (0.44 g, 0.89 mmol), prepared using a published procedure,[77] and 4-diphenylaminobenzaldehyde (0.55 g, 2.01 mmol) were dissolved in 80 mL of DMF and purged with Ar for 15 min. KO-*t*-Bu (0.50 g, 4.46 mmol) was then added, and the reaction mixture was refluxed for 30 min under Ar atmosphere. After being cooled to rt, the reaction was quenched with water. The precipitated product was filtered and recrystallized from toluene. The isolated product was further purified using dry-column vacuum chromatography[78] performed on silica gel 60 using gradient elution (*n*-heptane/$CHCl_3$) and recrystallized once more from benzene yielding 0.26 g (42%) of **$3_D(F_2)$** as a light green microcrystalline powder: mp >250 °C; ^{1}H NMR ($CDCl_3$) 7.49−7.35 (m, 6H), 7.32−7.22 (m, 10H), 7.17−7.00 (m, 14H), 6.95 (d, 2H, J = 16.6 Hz); ^{13}C NMR($CDCl_3$) 148.7, 147.5, 130.9, 129.4, 127.9, 125.0, 123.6, 123.0; ^{19}F NMR($CDCl_3$, 330 K) −141.7. Anal. Calcd for $C_{46}H_{32}F_4N_2\cdot(H_2O)_{1/2}$: C, 79.18; H, 4.77; N, 4.01. Found: C, 79.18; H, 4.55; N, 3.88.

Apparatus and Techniques. The details of the instrumentation and approach we use to produce and optically detect singlet oxygen in a two-photon experiment are presented elsewhere.[10] Likewise, the details of the approach we use to quantify singlet oxygen yields are presented elsewhere.[8]

In the experiment to quantify the relative reactivities of a given molecule to singlet oxygen, the independent sensitizer, C_{60}, was irradiated at 600 nm using the output of an optical parametric oscillator pumped by a Nd:YAG laser (Quanta-Ray GCR 230, MOPO 710). The experiment was performed at a pulse repetition rate of 10 Hz using an incident laser energy of 2.7 mJ/pulse and a beam that was 5 mm in diameter. The fullerene C_{60} was obtained from a commercial supplier and used as received.

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Supporting Information Available: NMR spectra of compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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