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Energy Transfer in the Azobenzene−Naphthalene Light Harvesting System

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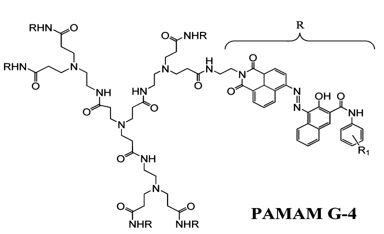
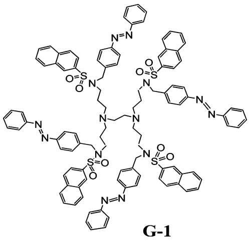
We have investigated the model light harvesting systems (LHSs) **A** and **B** typifying energy transfer (ET) between a naphthalene, Np (donor, **D**), and an azobenzene, Az (acceptor, **A**), shown schematically in Scheme 2. These models were actualized as the naphthyl azo molecules **1** and **4** containing a methylene tether (Scheme 1). The methoxy azo molecules **2** and **5**, respectively, served as benchmarks for the assessment of ET. Photophysical data, including initial rate constants for photoisomerization (trans to cis, *t*-**1** → *c*-**1**, and cis to trans, *c*-**1** → *t*-**1**), the relevant *c*-**1** → *t*-**1** quantum yields, and fluorescence quenching with free naphthalene, **3**, as **D** were measured. Therefore, (1) irradiation of **3** at (270 nm) to give **3*** generates fluorescence at 340 nm that is 65% quenched by the trans isomer of **2** (*t*-**2**) and 15% quenched by *c*-**2**. Comparable naphthalenic fluorescence of *c*-**1** (LH model **A**) is quenched beyond detectability. (2) Rates of photoisomerization were determined spectrophotometrically for *c*-**1** → *t*-**1** starting from the *c*-**1** photostationary state as compared with the *c*-**2** → *t*-**2** benchmark. (3) Progressing toward more complex LH systems, the initial rate constants, k_i, for *c*-**4** → *t*-**4** (LH model **B**), were measured as compared with the *c*-**5** → *t*-**5** benchmark. (4) A new criterion for ET (**D** → **A**) efficiency emerges that combines k_i (*c* → *t*) ratios and light absorption on irradiation (at 270 nm) ratios. On the basis of this new criterion, both **1** and **4** exhibit virtually quantitative ET efficiency. (5) Quenching data of **1** (almost complete) and **4** (95%) and ET are discussed by comparison with the relevant model azoarenes, **2** and **5**, respectively, and in terms of geometrical considerations. Implications for the extension of the results, notably the new criterion for ET efficiency, in these LH models **A** and **B** to the polymer and block copolymer $\mathbf{D}-(\mathrm{CRR'})_n-\mathbf{A}$ and $\mathbf{D}-(\mathrm{CRR'})_n-\mathbf{A}-(\mathrm{CR''R'''})_m-\mathbf{D}$ targets are considered.

Introduction

We have been engaged in a broad program of research in the area of materials chemistry,[1] and have applied, but also extended, our fundamental work on reactivity, stability, and properties of spiropyran−merocyanine systems[2] and, especially, azo/azoxy/hydrazoarenes,[3] including azo-modified PAMAM dendrimers up to the fourth generation.[3b−d] One thrust of this materials science work has been the investigation of model light harvesting systems (LHSs) with a view to design and synthesize polymer/copolymer LHS.



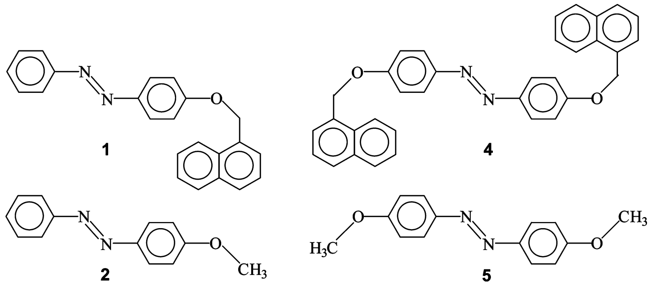
PAMAM G-4



G-1

Considerable interest has been elicited in all of the fundamental photochemical and photophysical processes involved in light harvesting: excitation and emission of donor (**D**) units, fluorescence quenching, energy transfer (ET), and so on.[4] The intensity of effort in this area is reflected in the range of authoritative reviews to appear lately.[5]

SCHEME 1



In simplified outline, donor (**D**) and acceptor (**A**) moieties are built into the target LH molecules. Irradiation by light of suitable wavelength will be absorbed ideally only by the **D** part, for example, naphththalenic, anthracenic units, coumarins,[6] and so on, and energy transferred from excited **D** (i.e., **D***) to **A** units of the LHS. ET should translate into a photophysical/photomechanical change that is reversible, that is, cyclable molecular work. Where this work involves two or potentially more discrete states, this component of an LHS can be viewed as a molecular switch. A range of molecular switches are being actively developed, including diarylethenes,[7] fulgides,[8] spiroox-

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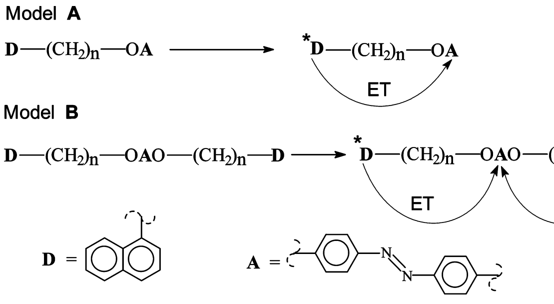
SCHEME 2



azines,[9] spiropyrans,[10] and acceptor (**A**) components in the light harvesting model systems of the present study, azobenzenes.[11]

In fact, azoarenes have proven to be useful acceptor components in molecular switching.[11,12] As but one of the many examples of the azoarene-functionalized systems examined, we note that Harbron et al.[13] studied the fluorescence modulation of semiconducting poly(phenylene vinylene) by pendent azobenzene molecules using steady-state and time-resolved fluorescence spectroscopy; the quenching efficiencies of the isomeric forms of the azo unit (cis and trans) differ significantly.

Supramolecular chemistry is another area where azobenzene acceptors (**A**) and naphthalenic donors (**D**) have found utility. A team led by Balzani, Raymo, Stoddart, and Williams has examined the host−guest complexation of a range of azobenzene-based acyclic and macrocyclic polyethers and catenanes in their trans (*t*) forms with the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene); irradiation induced isomerization to the cis (*c*) form, that is, *t* → *c* with concomitant dissociation of the supramolecular complex.[14] Fluorescence quenching involving the azobenzene-containing molecules and acyclic and macrocylic polyethers with built-in naphthalene moieties was also explored.

In another approach, Vögtle, Balzani, and coworkers prepared four generations, **G-1** through **G-4**, of the poly(propylene amine) family ($>N-(CH_2)_3-N<)_n(CH_2)_3-NH_2$; $n =$ number of repeating units) of dendrimers and functionalized the peripheral amines with both naphthalenic **D** units (as $-SO_2C_{10}H_7$) and *trans*-azobenzene **A** units (as $-CH_2PhN{=}NPh$), **G-1**.[15] The photophysical measurements on the dendrimer and model compounds are germane to the work reported herein and will be discussed later in this article.

The current study and results reported form a link in the chain of our development of light harvesting polymer/copolymer linear or regularly branched systems including, but not limited to, types abbreviated as **D**$-(CRR'-)_n-$**A**, **D**$-(CRR'-)_n-$**A**$-(-CR''R''')_m-$**D**, and so forth, where, for the simplest case, $R{=}R'{=}R''{=}R'''{=}H$ and the polymer is a polymethylenic homopolymer or block copolymer. In these cases, the chromogenic **D** and **A** functions are distal, contrasting with peripherally functionalized polymers of denser and more complex architectures where **D** and **A** may be adjacent or even geminal. Therefore, our basic model, *c*- and *t*-4-naphthylmethoxyazobenzene, **1**, consists of a naphthyl moiety (**D**) attached to an azobenzene (**A**) chromogen through a methylene spacer, **D**$-CH_2-$**A**, and in the current work, we assess ET from the donor chromophore to both isomeric (trans and cis) forms of the acceptor azo-unit, although we focus on the cis → trans (*c* → *t*) phototransformation (vide infra).

The comparison of the photophysical measurements for **1** is made with the baseline 4-methoxyazobenzene isomers (**2**) with free naphthalene (**3**) as the control system (Scheme 1). Progression of the work toward the goal of **D**$-(CRR')_n-$**A** polymeric LHS prompted scrutiny of 4,4′-bis(naphthylmethoxy)azobenzene, **4**, a **D**$-(CRR')_n-$**A**$-(CRR')_n-$**D** model. The photophysical data, including initial rate constants for *c* → *t* photoisomerization (i.e., *c*-**4** → *t*-**4**), are discussed with consideration of the baseline 4,4′-dimethoxyazobenzene, **5**, system as well as the other results. These systems (LH model **A** with benchmark **2** and LH model **B** with benchmark **5**) are shown in Scheme 1.

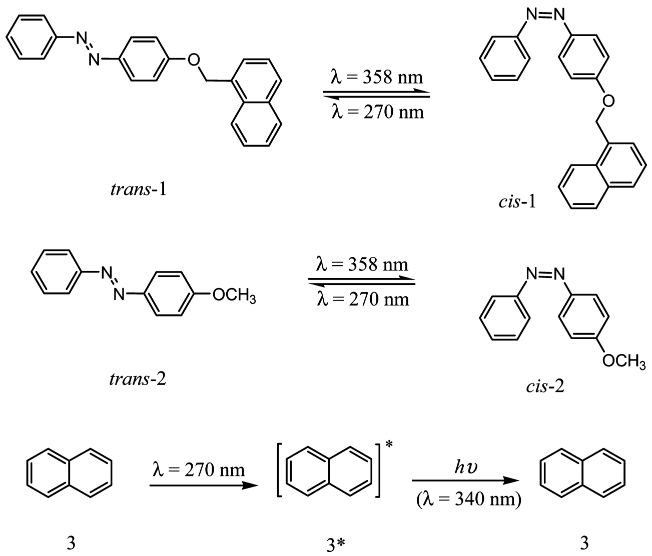


Figure 1. Photoisomerization processes *t* → *c* and *c* → *t* for **1** and **2** and excitation of naphthalene, **3**, to give **3*** and fluorescence of **3*** to give **3**.

A new criterion for assessment of ET in such systems emerges that combines kinetic and light energy absorption ratios (irradiation at 270 nm), and this ET efficiency criterion will be discussed. Implications for the overall goal of **D**$-(CRR')_n-$**A** and **D**$-(CRR')_n-$**A**$-(CR''R''')_m-$**D** polymer/copolymer LHS development will be considered in light of the present results.

Results and Discussion

Assessment of the efficiency of ET is a crucial first step in devising new LHS. To probe this fundamental requirement, light harvesting models **A** and **B** were constructed that contain naphthyl donor (**D**) and azobenzene acceptor (**A**) components. In principle, the former absorbs the relevant light energy and is excited to **D***, and ET occurs to **A**, as shown in Scheme 2.

In the evaluation of ET in LH models **A** and **B**, photophysical measurements are essential. Here donor units are naphthalene chromogens and acceptors are azobenzene moieties, and thus photosensitized isomerization (photoswitching) was expected. These measurements and the novel criterion for ET efficiency that arises from these data are the focus of these sections.

Therefore, compounds **1** (light harvesting model **A**) and **2** (benchmark) were prepared for the present study, and their structures and photoisomerism are illustrated in Figure 1, along with excitation of naphthalene, **3** to **3*** (and emission from **3***). Free naphthalene would be expected to model the donor naphthalenic moiety in **1** (and in **4**). Benchmark **2** is necessary for comparison with LH model **A** while also modeling the acceptor moiety of **1** and **4**.

In the following Section 1, we examine the UV−visible absorption spectra of **2** and **3** and the fluorescence emission of excited naphthalene, **3***, and demonstrate the spectroscopic compatibility of the individual chromogenic units that make up **1** and **4**.

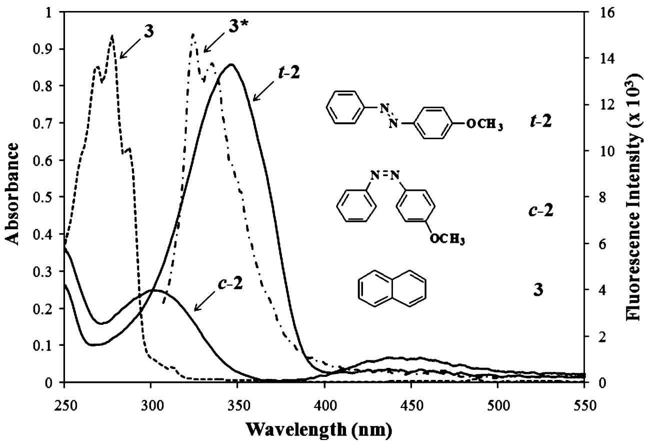


Figure 2. Absorption spectra of *t*-**2**, *c*-**2**, and **3** and fluorescence spectrum of **3*** in THF.

Further insights accrue from baseline experiments involving fluorescence quenching of **3*** (Figure 2) by **2**, as outlined in Section 2 below, whereas section 3 extends these quenching studies to LH model **A.**

Section 4 connects the quenching studies of *c*-**1** to the initial rate constants for photoisomerization that were determined for *t* → *c* and *c* → *t* processes for **1** and benchmark **2**, along with quantum yields. From these results, a new ET efficiency criterion emerges. Continuing studies, including application of the ET efficiency criterion, with analogous dinaphthyl compounds **4** (LH model **B**) and benchmark **5** that provide insight into potential polymeric LH systems, are discussed in Section 5.

1. Ultraviolet−Visible Absorption Spectra of *trans*-2 and *cis*-2 (*t*-2 and *c*-2) and Free Naphthalene, 3, and Fluorescence Emission of 3*. As can be seen in Figure 2, naphthalene, **3**, shows an absorption in the UV region (ca. 270 nm) and emission at ca. 340 nm; the vibrational fine structure of absorption and its almost mirror-image fluorescence band is typical of aromatics that do not undergo significant geometrical change upon excitation.[16] However, the absorbance of **3** falls in a region of minimum absorbance for either isomer of the model azobenzene, **2** (*t*-**2** and *c*-**2**). The spectroscopic compatibility thus demonstrated between the naphthalenic donor moiety in **1**, modeled by **3**, and the azobenzene acceptor chromogenic unit of **1**, modeled by **2**, clearly indicated that **1** (and the related **4**) would be a suitable light harvesting model system to study further.

The strong overlap of donor emission (**3*** as model for all naphthalenic units) and the absorbance for *t*-**2** led to the expectation of efficient ET in the trans-isomeric system, *t*-**1**. The less intense but still overlapping absorbance band of *c*-**2** suggested notable difference in behavior for *c*-**1** as compared with the trans counterpart, *t*-**1**.[13]

2. Quenching Studies: Free Naphthalene, 3, with *t*-2 and *c*-2. Excitation of **3** to **3***, as shown in Figure 2 and eq 1, can be followed by quenching processes in which the isomeric azoarenes, *t*-**2** and *c*-**2**, are excited by **3***; that is, energy transferred from **3*** should lead to the formation of [*t*-**2**]* and [*c*-**2**]*, respectively. These processes are shown in eqs 1−3

$$\mathbf{3} + h\nu(270\ \text{nm}) \rightarrow \mathbf{3}^* \tag{1}$$

$$\mathbf{3}^* + t\text{-}\mathbf{2} \rightarrow [t\text{-}\mathbf{2}]^* + \mathbf{3} \tag{2}$$

$$\mathbf{3}^* + c\text{-}\mathbf{2} \rightarrow [c\text{-}\mathbf{2}]^* + \mathbf{3} \tag{3}$$

When a solution in THF is prepared that contains 1 equiv of *t*-**2** ([*t*-**2**] = 3.0×10^{-5} M) relative to free **3** ([**3**] = 3.0×10^{-5} M), the fluorescence intensity of the band ascribed to emission from **3*** decreases in a process of quenching, as illustrated in Figure 3a. Compared with the fluorescence intensity in the absence of *t*-**2**, the quenching amounts to 65% (or apparent I_f/I'_f ca. 1.5) in this **3***/*t*-**2** system.

A significantly lower degree of quenching of the **3*** fluorescence is observed when the same experiment was performed using equimolar *c*-**2**, that is, **3***/*c*-**2** system ([*c*-**2**] and [**3**] = 3.0×10^{-5} M). Now the fluorescence intensity was decreased only 15% compared with the intensity observed in the absence of added *c*-**2** (or apparent I_f/I'_f ca. 6.6) (Figure 3b).

It is reasonable to presume that fluorescence quenching in these systems arises from the introduction of the *trans*- and *cis*-azobenzene compounds, as given in eqs 2 and 3. Less clear is the mechanism or even dominant mechanism of fluorescence quenching under these conditions. A wide range of mechanisms, radiative and nonradiative (including diffusional and static processes), are recognized, such as radiative and resonance energy transfer (RET).[17]

In general, ET processes are classified into two sets: (i) radiative mechanisms, where emission of a photon by a donor (**D**) is followed by reabsorption by an acceptor (**A**) and (ii)

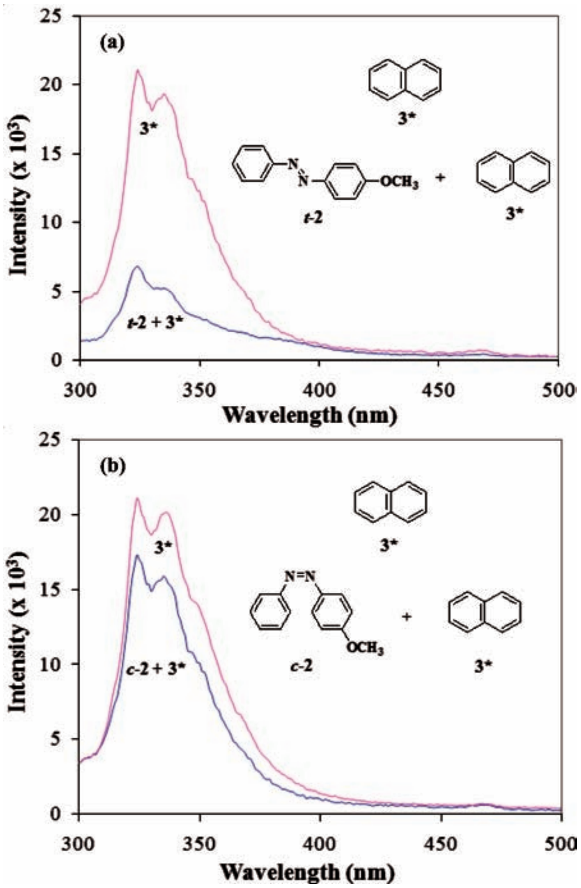


Figure 3. Fluorescence spectra of **3*** and **3*** with 1 molar equiv of (a) *t*-**2** (i.e., **3***/*t*-**2** system) and (b) *c*-**2** (i.e., **3***/*c*-**2** system). The reduction in fluorescence intensity at 340 nm represents (a) 65% and (b) 15% fluorescence quenching of **3*** by *t*-**2** and *c*-**2**, respectively. All concentrations were 3.0×10^{-5} M.

TABLE 1: Absorbance, Light Energy Absorption, Initial Rate Constants, and Quantum Yields from Irradiating *c*-1 and *c*-2 at 270 nm in THF[a]

process	*A* at 270 nm of cis isomer	light energy absorption at 270 nm[b]	k_i (s^{-1})[c]	quantum yields
c-**1** → *t*-**1** (LH model A)	0.359	0.56	5.35×10^{-4}	0.17
c-**2** → *t*-**2** (benchmark)	0.159	0.31	2.79×10^{-4}	0.17

[a] Concentrations are 3.0×10^{-5} M. [b] Light absorbed was calculated to be $1 - T$, where $T = 10^{-A}$. [c] Initial rate constant (k_i, where rate = k_i[cis]) is measured up to 5% completion of reaction. See the Experimental Section.

nonradiative mechanisms, which can be further categorized as either (a) Dexter, proceeding via a through bond process or (b) Förster, involving transition dipole−dipole interactions. The importance of Förster RET (i.e., FRET)[17] as a spectroscopic ruler[18] as well as in LH systems[19] has been well documented.[20] A reciprocal sixth power dependence of transfer efficiency upon the donor−acceptor distances is generally taken to implicate FRET as the dominant mechanism.[17] Extension of the current study to systems where the methylenic bridges separating donor and acceptor moieties are progressively extended may shed light on the mechanism of ET in these LH models (vide infra).

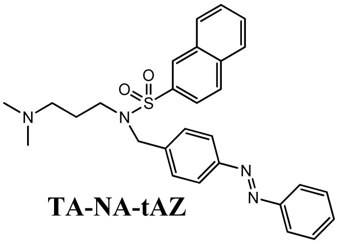
However, the salient point here is not that the mechanism for quenching in these systems was determined, for that was not an aim of the current study. Rather the quenching behavior in these model systems (**3***/*t*-**2** and **3***/*c*-**2**) forms the basis of comparison with the more complex model trans and cis isomers of **1**, where the naphthalenic donor moiety and its azobenzene counterpart are linked. We now proceed to our most basic **D**−**A** naphthalenic−azobenzene system **1** (LH model **A**).

3. Fluorescence Quenching for *c*-1 (LH Model A). *cis*-**1** combines both donor naphthalenic and acceptor azobenzene units. It is clear, nonetheless, from Figure 3b that **3*** in the **3***/*c*-**2** model system undergoes moderate quenching (15%), and the same is expected for *c*-**1**. What is observed for the *c*-**1** system is that UV irradiation at 270 nm yields no detectable emission. The close proximity of the donor and acceptor groups in this tethered system accounts for this result. The *c*-**1** system exhibits almost quantitative fluorescence quenching.

In quenching, energy is lost that otherwise would result in fluorescence emission. As in the **3***/*c*-**2** model, it is reasonable to involve the azobenzene chromogen of *c*-**1** as the acceptor of the energy, that is, the overall ET for this light harvesting model **A**. In the next section, the photoisomeric kinetic behavior of the azobenzene moiety of *c*-**1** will be considered.

4. Kinetics: Comparisons of Initial Rate Constants, k_i, Quantum Yields, and Absorbances. Kinetic investigation of photoisomerization was undertaken and comprises two parts. First, in each case, the trans isomer was irradiated at 358 nm (λ_{max} of azo moiety of *t*-**1** and *t*-**2**, Figure 1; also, Figure 2) remote from the region of the absorbance of the naphthyl unit (*t*-**1** or *c*-**1**), to generate the cis isomer. A photostationary state was reached, and the initial rate constants were evaluated. The second part involves irradiation of the two cis isomers (*c*-**1** and *c*-**2**) at 270 nm, which corresponds to λ_{max} of the naphthalenic unit of *c*-**1** and which falls within a region of low absorbance for *c*-**2**. All of the isomerization processes (*t* → *c*, *c* → *t*) followed first-order kinetics. (See the figures in the Supporting Information data. All first-order plots showed good linearity, $r^2 > 0.999$; See the Experimental Section). The light intensity of the Hg/Xe source was measured using ferrioxalate actinometry and found to be stable from day to day.[21]

The initial rate constants (k_i, s^{-1}) for *t* → *c* photoisomerization (*t*-**1** → *c*-**1** and *t*-**2** → *c*-**2**) upon separately irradiating the two trans isomers at 358 nm (Figure 1) were comparable; that is, *t*-**1** → *c*-**1**, $k_i = 2.55 \times 10^{-3}$ s^{-1} and *t*-**2** → *c*-**2**, $k_i = 2.26 \times 10^{-3}$ s^{-1} (Figures S1 and S2 in the Supporting Information). This result is in accord with the report by the Vögtle−Balzani groups for the TA−NA−*t*-Az model for peripherally **D**- and **A**-substituted poly(propylene amine) dendrimers (vide supra):[15] (a) the photoisomerization behavior of the Az chromogen of this model was almost identical to that of 4-methyl-azobenzene; (b) quenching of the NA moiety fluorescence was efficient but did not lead to sensitization of the *t* → *c* photomerization; and (c) the *c* → *t* process is selectively sensitized. Whereas the TA−NA−*t*-Az model is specific to evaluation of the poly(propylene amine) dendrimeric LH system that exhibits electron transfer as well as ET pathways for fluorescence quenching, selective *c* → *t* azobenzene component sensitization has been observed in other related systems.[22](Also see ref 13.) On these grounds, the focus of the current work was set on the *c* → *t* phototransformation. The possibility of competitive electron transfer in the present LH models will be discussed in Section 5.



TA-NA-tAZ

Turning to the cis isomers at initial concentration of 3.0×10^{-5} M, Table 1 shows differing initial rate constant, k_i, values (*c*-**1** → *t*-**1** and *c*-**2** → *t*-**2**). The initial photoisomerization rate constant is k_i. The ratio of k_i for *c*-**1** (i.e., *c*-**1** → *t*-**1**) as compared with k_i for *c*-**2** (i.e., *c*-**2** → *t*-**2**) is 1.9.

$$\frac{k_i(c\text{-}1 \rightarrow t\text{-}1)}{k_i(c\text{-}2 \rightarrow t\text{-}2)} = 1.9$$

The similarity in the k_i for *t*-**1** (*t*-**1** → *c*-**1**) as compared with *t*-**2** (*t*-**2** → *c*-**2**), vide supra, that contrasts with the factor of 1.9 found in the corresponding comparison of k_i values for *c*-**1** (i.e., *c*-**1** → *t*-**1** versus *c*-**2** → *t*-**2**) further focused attention on the *c* → *t* photoisomerization processes. These systems are highlighted hereafter.

Significantly, the quantum yields (Table 1) for the *c* → *t* photoisomerization are the same. If irradiation at 270 nm results in excitation of the naphthyl unit of *c*-**1** and fluorescence quenching occurs through nonradiative decay or any other mechanism that does not involve the azo part of **1**, then it would follow that the quantum yield for the *c*-**1** → *t*-**1** process should be lower than that for benchmark **2**, (*c*-**2** → *t*-**2**). In the case where lower *c*-**1** → *t*-**1** quantum yield is observed, the naphthalenic unit would be behaving as a light harvester but not effectively transferring energy to the azo unit. Recall that

TABLE 2: Light Energy Absorption, Initial Rate Constants, and Quantum Yields from Irradiating *c*-1 and *c*-2 at 270 nm in THF[a]

process	light energy absorption at 270 nm[b]	k_i (s^{-1})[c]	quantum yields
c-**1** → *t*-**1** (LH model A)	0.85	4.14×10^{-4}	0.19
c-**2** → *t*-**2** (benchmark)	0.53	2.65×10^{-4}	0.19

[a] Concentrations are 7.0×10^{-5} M. [b] Light absorbed was calculated to be $1 - T$, where $T = 10^{-A}$. [c] Initial rate constant (k_i, where rate = k_i[cis]) is measured up to 5% completion of reaction. See the Experimental Section.

at 270 nm, *c*-**2** absorbs only weakly; **3** absorbs more intensely here. We recognize the difficulties identified in using quantum yields solely to assign efficiencies with regard to azoarene-containing compounds.[15] Notwithstanding these difficulties, the observation that the quantum yields for *c* → *t* isomerization are the same for *c*-**1** LH model **A** and benchmark *c*-**2** accords with the idea that light energy absorbed by the naphthalenic moieties of *c*-**1** is transferred to the azobenzene chromogen with high efficiency (close to 100%).

Note that at 270 nm, the starting reactants (*c*-**1** and *c*-**2**) absorb differently (Figures S7 and S8 in the Supporting Information); this difference should be accounted for. Clearly, absorbance data in Table 1 shows that *c*-**1** ($A = 0.359$) absorbs more strongly at this wavelength than *c*-**2** ($A = 0.159$), which is consistent with the presence of the naphthyl chromogen in *c*-**1** and not in *c*-**2**. As a measure of the light energy entering the system, the absorbance $1 - T$ (Table 1) indicates that more energy enters *c*-**1** than *c*-**2**; the ratio of these light energy values for *c*-**1** as compared with those for *c*-**2** is strikingly similar to the ratio of the initial rate constants, k_i, for the same photoisomerizations, that is, both 1.9, within experimental error. This further leads us to believe that ET is occurring with practically 100% efficiency.

To test the reproducibility of our observation that the ratio of initial rate constants equals the ratio of light energy absorption at 270 nm for LH model **A** as compared with *c*-**2** as the benchmark, the measurements were repeated using a different concentration of the two azoarenes, **1** and **2**. Accordingly, Table 2 shows the results obtained when a concentration of 7.0×10^{-5} M of **1** and **2** was used. The absorbances for *c*-**1** and *c*-**2** at 270 nm were recorded as 0.836 and 0.328, respectively; the higher absorbance for *c*-**1** is ascribable to the presence of the naphthyl moiety. This yields the ratio of light energy absorption at 270 nm (0.85/0.53, calculated as above) to be 1.6, again equal to the ratio of the initial rate constants ((k_i LH model **A**)/(k_i benchmark **2**) = $(4.14 \times 10^{-4})/(2.65 \times 10^{-4}) = 1.6$), taking into account experimental error. Therefore, reproducibility has been demonstrated and, importantly, the combined ratio (1.6/1.6 = 1.0) has been shown to constitute a consistent criterion for ET efficiency.

Note once again that the quantum yield for both systems is the same. As discussed above, the quantum yield for *c*-**1** as compared with that for *c*-**2**, should be lower rather than the same if light energy was not transferred efficiently to the azobenzene acceptor.

Taken altogether, quantum yield, rate constants for *c* → *t* isomerization, and absorbance measurements at 270 nm all support the view that light harvested by the naphthyl moiety is transferred to the azobenzene and sensitizes photoisomerization. This leads us to define a new criterion for the efficiency of ET: the ratio of the initial rate constants for the photoisomerization process for *c*-**1** as compared with that for benchmark *c*-**2** relative to the ratio of light energy absorption upon irradiation at 270 nm (as per Table 1) for *c*-**1** as compared with that for *c*-**2.**

5. Assessment of Potential Competitive Electron Transfer in LH Models A and B. It is germane in our discussion to consider electron transfer to be a competitive process in the present *t*-**1** and *c*-**1** systems and, by extension, in the *c*-**4** system (LH model **B**, vide infra). The analysis distils down to the question: Is electron transfer from the naphthalenic moiety to either the *trans*- or *cis*-azobenzene chromogen spontaneous? If independent naphthalene and azobenzene molecules are deemed suitable analogues for *t*-**1** and *c*-**1**, then the criterion of spontaneity could be assessed from data for the standard half-cell potentials for single electron oxidation of naphthalene (Np) to give the naphthalene radical cation ($\mathrm{Np}^{+\cdot}$) and for single electron reductions of *trans*- and *cis*-azobenzene to give the respective azobenzene radical anions ($\mathrm{Az}^{-\bullet}$). In other words, the process shown in eq 4 approximates that of eq 5, where a diradical zwitterion is the putative product

$$\mathrm{Np} + \mathrm{Az} \rightarrow \mathrm{Np}^{+\bullet} + \mathrm{Az}^{-\bullet} \tag{4}$$

$$1 \rightarrow {}^{+\bullet}\mathrm{Np{-}CH_2{-}O{-}Az}^{-\bullet} \tag{5}$$

The process is spontaneous if $E_{\mathrm{cell}}{}^0$ derived from the two standard half-cell potentials is positive.

The electrochemical data (e.g., combined cyclic voltammetry with ESR for identification of the paramagnetic species) for the oxidation half-cell for naphthalene show that $\mathrm{Np}^{+\bullet}$ formed in the anodic cycle interacts with free Np in solution to give a dimeric radical cation of the π-stacking type[23]

$$\mathrm{Np} + \mathrm{Np}^{+\bullet} \rightarrow \mathrm{Np}\cdots\mathrm{Np}^{+\bullet} \tag{6}$$

Substituted naphthalenes such as 1,4-dimethylnaphthalene are sterically buttressed against such dimerization and may be an appropriate alternative model to Np in eq 4. Although no $E_{1/2}{}^{\mathrm{ox}}$ (approximating $E_{\mathrm{ox}}{}^0$) data have been reported for 1,4-dimethylnaphthalene in THF, the solvent of the current study, the mean of values determined in dichloromethane (two separate measurements)[23,24] and aqueous acetone[25] corrected to the standard hydrogen electrode (SHE)[26] is +1.4 V.

Grampp and coworkers,[27] using photomodulated voltammetry,[28] reported the $E_{1/2}{}^{\mathrm{ox}}$ for *cis*- and *trans*-azobenzene in a range of polar aprotic solvents and provided linear correlation equations relating $E_{\mathrm{red}}{}^0$ to the Kamlet, Abboud, Abraham, and Taft (KAAT) solvent parameter, π^*.[29] Via these correlations, $E_{\mathrm{red}}{}^0$ for *cis*- and *trans*-azobenzene in THF, corrected to SHE,[26] are −1.7 and −1.5 V, respectively.

Overall, by these estimates, $E_{\mathrm{cell}}{}^0$ would be negative for single electron transfer from 1,4-dimethylnaphthalene to both *cis*-azobenzene ($E_{\mathrm{cell}}{}^0 = E_{\mathrm{ox}}{}^0 + E_{\mathrm{red}}{}^0 = +1.4 - 1.7 = -0.3$ V) and *trans*-azobenzene ($E_{\mathrm{cell}}{}^0 = E_{\mathrm{ox}}{}^0 + E_{\mathrm{red}}{}^0 = +1.4 - 1.5 = -0.1$ V). Therefore, within the limitations of the extant data, electron transfer in **1** appears to be thermodynamically unfavorable (eq 5).

6. Proceeding toward Polymer Light Harvesting Systems (LH Model B). Progressing from **1**−**4**, that is, from LH model **A** to LH model **B** (Figure 4), one proceeds in the direction of design of polymer LHSs, the most successful of which mimic photosynthetic systems.[5b,30b] In general, such LH systems include an array of (usually) peripheral light harvesting moieties that

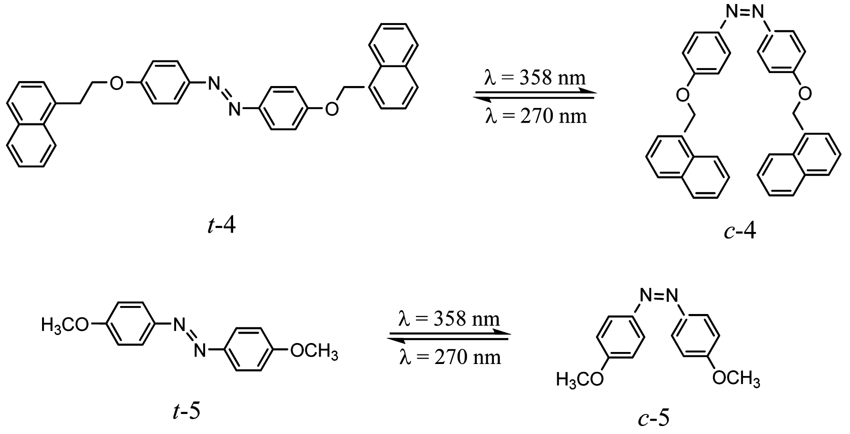


Figure 4. Photoisomerization processes *t* → *c* and *c* → *t* for **4** and **5**.

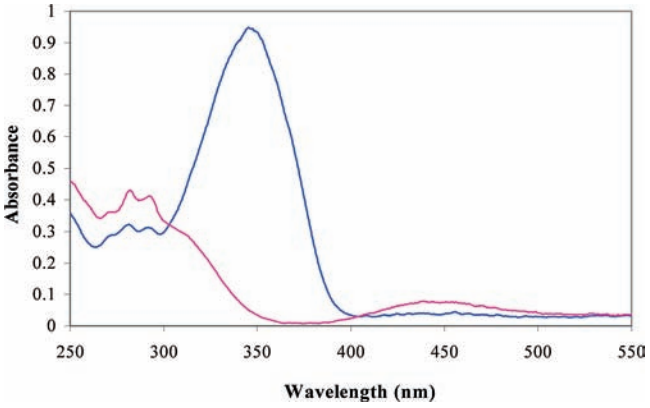


Figure 5. Absorption spectra of *c*-**4** and *t*-**4** in THF.

TABLE 3: Light Energy Absorption and Initial Rate Constants from Irradiating *c*-4 and *c*-5 at 270 nm, in THF[a]

process	light energy absorption at 270 nm[b]	k_1 (s^{-1})[c]
c-**4** → *t*-**4** (LH model B)	0.75	3.95×10^{-4}
c-**5** → *t*-**5** (benchmark)	0.41	2.18×10^{-4}

[a] Concentrations are 3.0×10^{-5} M. [b] Light absorbed was calculated to be $1 - T$, where $T = 10^{-A}$. [c] Initial rate constant (k_i, where rate = k_i[cis]) is measured up to 5% completion of reaction. See the Experimental Section.

funnel the energy to relatively few energy acceptor units.[30] Compared with **1**, **4** contains two *para*-naphthylmethoxy groups or, naively, two light harvesting functions linked to the central azobenzene chromogen. Auxochromic groups such as these naphthylmethoxyls modify the base chromogenic absorption spectrum (e.g., batho-, hypo-, hypso-, and hyperchromic shifts in some bands). Therefore, the appropriate model azoarene for comparison with **4** (as in *c* → *t* initial rates) would reasonably be benchmark **5** that bears both 4- and 4′-methoxyls.

When the standard fluorescence quenching experiment was performed (irradiate 270 nm, observe fluorescence 340 nm; cf., absorption spectra of *t*-**4** and *c*-**4**, Figure 5), the results showed 95% quenching for *c*-**4**, that is, just detectable. This compares with practically complete quenching in the *c*-**1** case, where only one naphthyl moiety is present.

On one hand, if quenching is strongly controlled by geometry in *c*-**4**, then it might be argued that only one naphthyl unit could be involved at a given time; a statistical 50% quenching should result, rather than the 95% observed. On the other hand, if each naphthyl unit is treated as being totally independent, then each would approach the state of free naphthalene, as found in the **3***/*c*-**2** quenching system. Here a 15% quenching of **3*** was found. Again, treating each naphthyl moiety as a free naphthalene should give about 30% quenching overall; 95% is found in the current *c*-**4** system, which is consistent with the fact that donors and acceptor are tethered in close proximity here. It is further notable that when the quenching experiment is performed with 2 molar equiv of free naphthalene relative to the concentration of the benchmark *cis*-azoarene **5**, which is a surrogate for the azo moiety of **4**, the fluorescence quenching amounts to 44% (Figure not shown) in this system; 95% is found in the current *c*-**4** case. We conclude that the geometrical constraints on ET from the naphthyl moieties in *c*-**4** are such that quenching is slightly diminished to 95%, close to the almost total quenching found in the corresponding *c*-**1** system. It can be seen that LH models **A** and **B** are characterized by high ET efficiency.

By applying our composite criterion to the *c*-**4** → *t*-**4** as compared with the *c*-**5** → *t*-**5** photoisomerization, it can be seen from Table 3 that the initial rate constant (k_i) ratio and the absorbance (1 − *T*) ratio are again the same within experimental limits, that is, 1.8. This is in accord with the other systems where ET efficiency was almost quantitative.

Conclusions

The current study shows: (1) A composite criterion for assessing ET efficiency in naphthyl-linked−azoarene light-harvesting systems emerges that combines ratios of initial rates of photoisomerization (k_i for *c* → *t*) with the light energy absorption ratio in the donor (naphthalenic region) in one overall ratio. An overall ratio of unity indicates virtually complete ET. Quantum yields provide further support for this criterion of efficiency in ET. (2) Observation of moderate quantum yields in the photosensitized isomerization (*c* → *t*) in the current systems indicates that future LH models for study should include higher loading of donor groups. (3) For *cis*-4-naphthylmethoxyazobenzene (*c*-**1,** LH model **A**), the *c* → *t* isomerization initial rate constants and light energy absorption ratio assign almost quantitative ET here. (4) For *cis*-4,4′-bis(napthylmethoxy)azobenzene (*c*-**4,** LH model **B**), a model along the path to polymeric light harvesters, the composite criterion suggests close-to-quantitative ET. (5) Further work will be required to demonstrate the generality of this new criterion for ET efficiency that combines the ratio of light energy absorption with the rate constant ratio. (6) Geometrical constraints affect fluorescence quenching in models such as *c*-**4** and point in the direction of expanding the methylene bridge of **1** and **4** (i.e., to $-[CR_2]_n-$) to construct more versatile LHSs, bridging the gap to controlled architecture polymeric systems.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or Avance-400 (automatic sample changer, BB auto tuning) spectrometer. Mass spectroscopic analysis was performed using electron impact (EI), chemical ionization (CI), and electrospray ionization (ESI). Melting points (uncorrected) were measured using a Fisher−Johns melting point apparatus.

The light harvesting experiments were conducted using a S2000 miniature fiber optic spectrophotometer from Ocean Optics (Dunedin, Florida) connected to a four-way temperature-controlled cuvette holder from Quantum Northwest (Spokane, Washington) via 400 μm optical fibers to measure the absorbance. The irradiation source was a 200 W Hg/Xe lamp attached to a model 101 0.2 m f/4 monochromator equipped with a 1200 g mm^{-1} 300 nm blaze standard grating from Photon Technology International connected to the cuvette holder via a 10 mm quartz fiber bundle. Data were collected by means of 001Base32 software. The light intensity of the Hg/Xe irradiation source was measured using ferrioxalate actinometry and was found to be stable from day to day.[21]

Starting materials and inorganic reagents for the preparation of compounds **1**−**5** were obtained commercially in the highest purity available and were used without further purification. Reagent grade or higher purity solvents were used as purchased. Tetrahydrofuran (THF) for photophysical measurements was dried over sodium wire and distilled and stored under nitrogen.[31]

4-Naphthylmethoxyazobenzene (1). Compound **1** was prepared by reaction of 4-hydroxyazobenzene with 1-(chloromethyl)naphthalene under mildly basic conditions. A mixture of *p*-hydroxyazobenzene (2.39 g, 12.1 mmol), 1-(chloromethyl)-naphthalene (2.70 g, 15.3 mmol), anhydrous K_2CO_3 (4.17 g, 30.2 mmol), and 18-crown-6 (0.66 g, 2.42 mmol) in dry acetone (50 mL) was refluxed under nitrogen for 24 h. After the removal of solvent at reduced pressure (rotary evaporation), the residue was dissolved in CH_2Cl_2 (50 mL) and extracted with water (3 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The solid was recrystallized from CH_2Cl_2/hexanes to yield orange crystals of *t*-**1** (3.00 g, 74%). mp 127−128 °C. ^{1}H NMR ($CDCl_3$, δ): 8.09 (1H, d, 7.80 Hz), 7.98 (2H, d, 8.60 Hz), 7.91 (2H, d, 7.70 Hz), 7.99−7.90 (2H, m), 7.66−7.45 (7H, m, 3H′s), 7.20 (2H, d, 8.60 Hz), 5.61 (2H, s). ^{13}C NMR ($CDCl_3$, δ): 161.30, 152.77, 147.27, 133.83, 131.75, 131.49, 130.44, 129.27, 129.06, 128.80, 126.75, 126.62, 126.04, 125.35, 124.82, 123.60, 122.60, 115.19, 68.98. TOF−EIMS *m*/*z*: 338.1423 (calcd for $C_{23}H_{18}N_2O$, 338.1419).

4,4′-Dihydroxyazobenzene. This compound was prepared by the method reported by Tomohiro and coworkers[32] on the basis of the earlier procedure of Willstätter and Benz[33] via reaction of the nitro group of 4-nitrophenol in hot concentrated aqueous KOH. Products were poured in cold water and acidified (HCl), and the crude 4,4′-dihydroxyazobenzene was isolated from the ether extracts. Recrystallized from 1:1 (v/v) ethanol/H_2O: Yield 69% (lit. 43%).[29] mp 226−227 °C. NMR data is comparable to that reported for 4,4′-dihydroxyazobenzene, determined in perdeuteriodimethyl sulfoxide.[32] ^{1}H NMR ($CDCl_3$, δ): 9.14 (2H, s), 7.80 (4H, dd, 4.70 Hz), 6.99 (4H, dd, 4.60 Hz). ^{13}C NMR ($CDCl_3$, δ): 159.97, 146.24, 124.27, 115.69. CI−MS: $(M + H)^+$ 214.95 (calcd for $C_{12}H_{10}N_2O_2$, 215.08).

4,4′-Bis(naphthylmethoxy)azobenzene (4). Compound **4** was synthesized via reacting 4,4′-dihydroxyazobenzene with 1-(chloromethyl)naphthalene. A mixture of 4,4′-dihydroxyazobenzene (0.20 g, 0.94 mmol), 1-(chloromethyl)naphthalene (0.41 g, 2.33 mmol), anhydrous K_2CO_3 (0.32 g, 2.33 mmol), and 18-crown-6 (0.03 g, 0.469 mmol) in dry acetone (50 mL) was refluxed under nitrogen for 24 h. The reaction was terminated by rapid cooling. The precipitate was recrystallized from CH_2Cl_2/hexanes and dried under vacuum to yield orange crystals of *t*-**4**, (0.30 g, 65%). ^{1}H NMR ($CDCl_3$, δ): 8.09 (2H, dd, 7.8 Hz), 7.94 (4H, dd, 8.60 Hz), 7.95−7.90 (4H, m), 7.66−7.49 (8H, m), 7.19 (4H, dd, 9.10 Hz), 5.61 (4H, s). ^{13}C NMR ($CDCl_3$, δ): 160.87, 147.32, 133.82, 131.84, 131.49, 129.23, 128.78, 126.73, 126.59, 126.02, 125.35, 124.46, 123.62, 115.17, 68.95. TOF−EIMS *m*/*z*: 494.2004 (calcd for $C_{34}H_{26}N_2O_2$, 494.1994).

4,4′-Dimethoxyazobenzene (5). Displacement of iodide from methyl iodide by 4,4′-dihydroxyazobenzene under alkaline conditions yielded 4,4′-dimethoxyazobenzene, **5**. A mixture of 4,4′-dihydroxyazobenzene (0.50 g, 2.34 mmol), methyl iodide (0.83 g, 5.85 mmol), anhydrous K_2CO_3 (0.80 g, 5.80 mmol), and 18-crown-6 (0.12 g, 0.44 mmol) in dry acetone (50 mL) was refluxed under argon for 24 h. After removal of solvent by rotary evaporation, the residue was dissolved in CH_2Cl_2 (50 mL) and extracted with water (3 × 50 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The solid was recrystallized from CH_2Cl_2/hexanes to yield orange crystals of *t*-**5** (0.45 g, 80%). mp 165−166 °C. ^{1}H NMR (acetone-d_6, δ): 7.87 (4H, d, 6.90 Hz), 7.08 (4H, d, 6.90 Hz), 3.89 (6H, s). ^{13}C NMR (acetone-d_6, δ): 161.93; 146.87; 124.18; 114.27; 55.10. ES−MS *m*/*z*: 243.1152 (calcd for $C_{14}H_{14}N_2O_2$, 242.1100).

Light Harvesting. ***a. Kinetics.*** The $c \rightarrow t$ and the $t \rightarrow c$ isomerization processes were followed upon irradiation of solutions of the azo compounds in anhydrous THF at 270 nm ($\lambda_{\max}$ of the naphthalene moiety) on the Ocean Optics UV/vis spectrophotometer setup, and they obeyed first-order kinetics. For isomerization of the cis form to its trans counterpart, rate $= \mathrm{d[trans]}/\mathrm{d}t = k_i[\mathrm{cis}]$, where the reaction was monitored up to only 5% of the reaction, that is, the initial portion of the reaction (ca. 600 s; cf. Figures S1 and S2 of the Supporting Information). To examine the $c \rightarrow t$ isomerization process at 270 nm, we first irradiated the trans isomers at 358 nm to obtain the cis isomer at the photostationary state. To study the $t \rightarrow c$ isomerization process, we directly irradiated the trans isomers at 270 nm. For either first-order process, the usual linear plot of $\ln[A_{\mathrm{inf}} - A]$ versus time yields r^2 values of >0.999.

b. Fluorescence. Steady-state fluorescence measurements were carried out using a Perkin-Elmer fluorescence spectrophotometer on both the cis and trans isomers of the control compounds (**2** and **5**) with free naphthalene (**3**) as well as on both isomeric forms of the light harvesting compounds (**1** and **4**) with excitation at 270 nm. All concentrations used were 3.0×10^{-5} M, except for one control experiment (Table 2) where the concentrations were 7.0×10^{-5} M. All solutions were prepared in anhydrous THF.

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Supporting Information Available: First-order plots (initial rate constants) for $t \rightarrow c$ and $c \rightarrow t$ photoisomerization of **1** and time-dependent absorption spectra of *c*-**1** and *c*-**2** upon irradiation at 270 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

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