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Synthesis of novel rigid-rod and tripodal azulene chromophores

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Abstract—Two novel azulene chromophores **1** and **2** were synthesized to study dynamics of ultrafast electron injection at the interface of TiO_2 semiconductor nanoparticles. Fluorescence quenching was observed upon binding.

Azulene and its derivatives possess unusual electronic and optical properties and find application as components in advanced materials.[1,2] In particular, azulene has a long-lived (1.4 ns) emissive second excited singlet (S_2) state and an extremely short-lived (1.6 ps) nonemissive first excited singlet (S_1) state, the rapid nonradiative relaxation of which is attributed to the presence of a conical intersection between the S_1 and S_0 states.[3] For this reason, azulene was selected to study electron transfer into TiO_2 from vibrationally nonrelaxed excited states (Fig. 1a). The rates of injection and recombination from 1-carboxyazulene directly bound to TiO_2 nanoparticles and azulene encapsulated within a host molecule (hemicarceplex) anchored to TiO_2 were recently studied.[4] In the case of the directly bound 1-carboxyazulene injection from the S_2 state was complete within 100 fs.[4] In the case of the encapsulated azulene the injection and recombination rates are reduced by approximately 3-orders of magnitude.[4]

In this letter, we describe the synthesis and properties of two novel azulene chromophores that bind to TiO_2 nanoparticles through a rigid-rod (**1**) or a tripodal (**2**) linker. Compounds **1** and **2** were designed as models to study the effects of linkers on electron injection of azulene into TiO_2 as illustrated in Figure 1b.

Rigid-rod **1** was synthesized by the two routes shown in Scheme 1.

Route A involved Suzuki-type[5] coupling of dimethyl-5-iodo-isophthalate **5b** with 2-bromoazulene **7** (Scheme 2), to afford rigid-rod **1** in 35% yield. In this reaction, instead of the commercially available dimethyl-5-bromo-isophthalate, we used the more reactive iodoisophthalate **4**,[6] which was readily prepared from the diazonium salt of the aminoderivative **3**. The poor overall yield of **1** (~8% from **3**) from this method, which was previously employed for the synthesis of other rigid-rods,[7] prompted us to use route B as an alternative.

Rigid-rod **1** was synthesized in 74% yield by Sonogashira[8] cross-coupling of **4** and 2-ethynylazulene[9] **7b** (Scheme 3). Ethynylazulene was synthesized in high yield upon iodination of azulene with *N*-iodosuccinimide (NIS) followed by cross-coupling with trimethylsilyacetylene. From this route, the overall yield of **1** from **3** was 23%. Two different cross-coupling methodologies were used in the final step (Suzuki in route B and Sonogashira in route A) because Suzuki-type coupling, proceeds through an ethynylboronate intermediate formed by reaction of the lithium acetylide of **5b**, and prevents the dimerization of **5b**. The dimerization of the highly reactive ethynylazulene **7b** in Sonogashira conditions was minimal and the cross-coupling with **4** proceeded in high yields.

The same strategy, route B involving Sonogashira cross-coupling of the linker with the ethyne-substituted chromophore, was used to synthesize azulene-tripod **2** (Scheme 4), instead of route A, which we have prevalently followed for the synthesis of tripodal dyes.[10] Carboxylation of 1,3,5,7-tetrakis-(*p*-iodophenyl)adamantane **8**[11] with *t*-BuLi/CO_2, esterification with diazomethane and separation of the di-, tri-, and tetrasubstituted compounds by silica gel column chromatography gave

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Keywords: Semiconductor nanoparticles; Rigid-rod linkers; Tripodal linkers.

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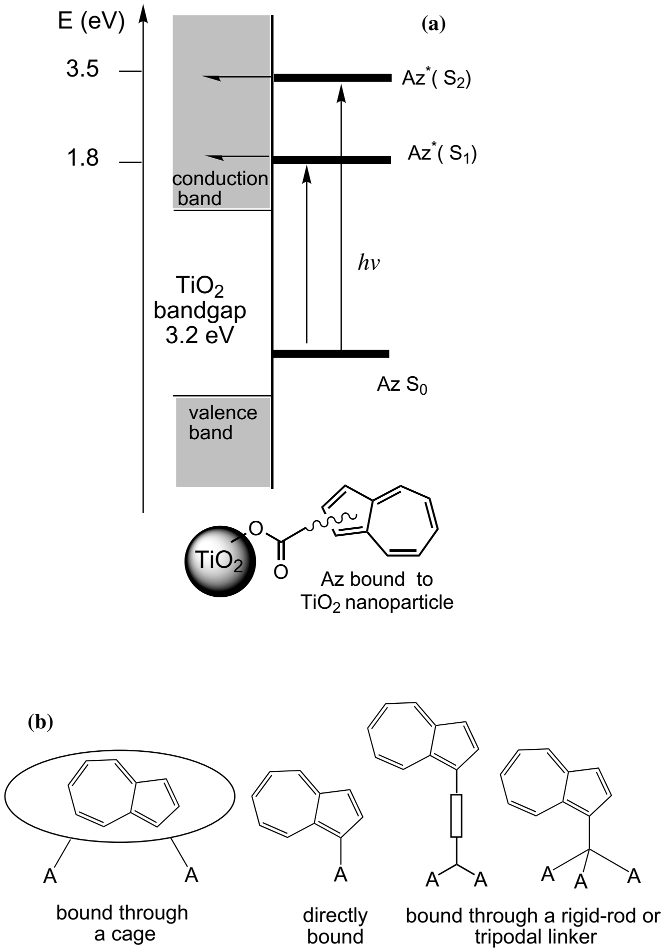
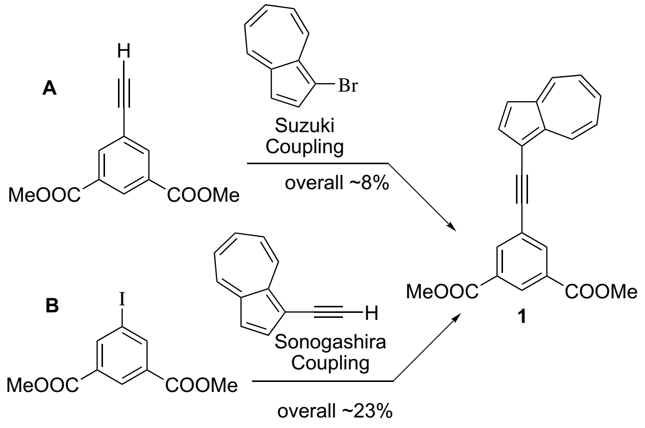


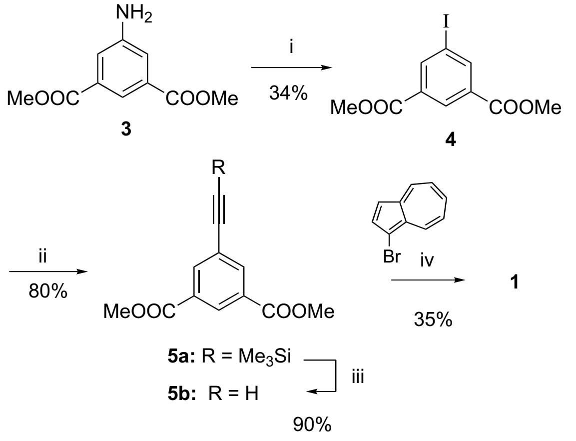
Figure 1. (a) Electron injection into TiO_2 nanoparticles from the bound photoexcited azulene (Az*). (b) Models used to study this process: azulene bound through different types of linkers. A = COOH anchoring group.



Scheme 1. Synthetic routes to azulene rigid-rod **1**.

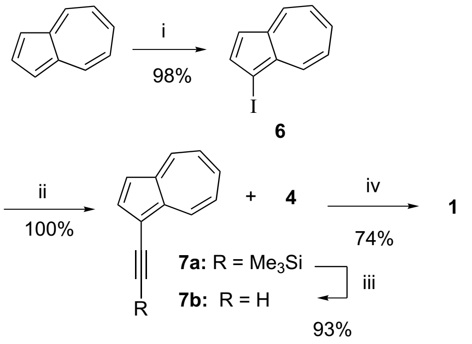
monoiodide **9** in 6–10% yields.[12] Sonogashira cross-coupling of **9** with 2-ethynylazulene **7b** gave **2** in 37% yield.

While azulene derivatives **6** and **7b** easily decomposed and were used immediately, both **1** and **2**, isolated as green powders, were remarkably stable.[13] Their spectral properties are reported in Table 1. The absorption spectra of **1** and **2**, where azulene is substituted with a *p*-ethynylenephenylene group, showed a significant



Scheme 2. Synthesis of **1** by route A. Reagents and conditions: (i) (a) $NaNO_2$, HCl (aq), −6 to −3 °C; (b) KI, toluene, −6 to 0 °C, (c) 12 h at rt, (d) 1 h at reflux; (ii) $PdCl_2(PPh_3)_2$, CuBr, *i*-Pr_2NH, TMSA, reflux 24 h; (iii) TBAF, THF, 2 h at rt; (iv) $Pd(PPh_3)_4$, $(TMS)_2NLi$, MeO-9-BBN, THF.

(60 nm) red shift of the $S_0 \rightarrow S_2$ band compared to unsubstituted azulene. The weaker $S_0 \rightarrow S_1$ lower energy band, responsible for the blue color of unsubstituted azulene, was also red shifted by ~30 nm in **1** and **2**.



Scheme 3. Synthesis of **1** by route B. Reagents and conditions: (i) NIS, CH_2Cl_2, 2 h at rt; (ii) TMSA, $Pd(dba)_2$, CuI, *i*-Pr_2NH, PPh_3, toluene, 24 h at rt; (iii) KOH in MeOH/THF (1:1), 4 h at rt; (iv) $Pd(dba)_2$, CuI, *i*-Pr_2NH, PPh_3, toluene, 24 h at rt.

The methyl esters **1** and **2** were converted into the corresponding carboxylic acids (**1-COOH** and **2-COOH**)[14] and added to diluted (250 or 500 mg/L) colloidal EtOH solutions[4] of TiO_2 nanoparticles. The colloidal solutions (pH ~ 3) were optically transparent and light scattering was minimal.[15] The ground state absorption spectra of **1-COOH** and **2-COOH** did not change considerably upon binding (~2 nm red shift), as shown in Figure 2. The absence of charge transfer bands or large shifts upon binding suggests weak electronic coupling of the azulene unit with the semiconductor.

The fluorescence emission of the azulene chromophores was clearly quenched by addition of TiO_2 (Fig. 3), indicating that the molecules bind to the nanoparticles and that binding results in electron injection in the semiconductor. The residual fluorescence is likely to originate entirely from nonbound molecules.

Table 1. Absorption and fluorescence solution data for **1**, **2**, and azulene

Chromophore	λ_{max}, nm		λ_F, nm
	$S_0 \rightarrow S_2$ (ε_{401}, M^{-1} cm^{-1})	$S_0 \rightarrow S_1$	
Azulene[a]	340	572	373
1[b]	401 (9964)	598	429
2[b]	402 (8216)	600	425

[a] MeOH, 1×10^{-4} M.

[b] EtOH, 2.5×10^{-5} M.

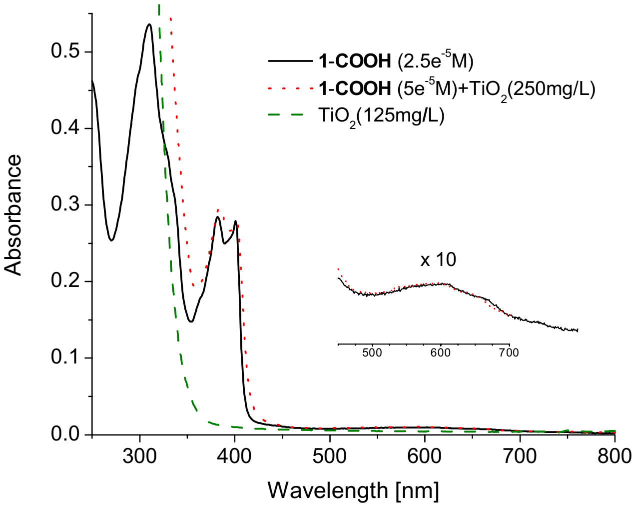
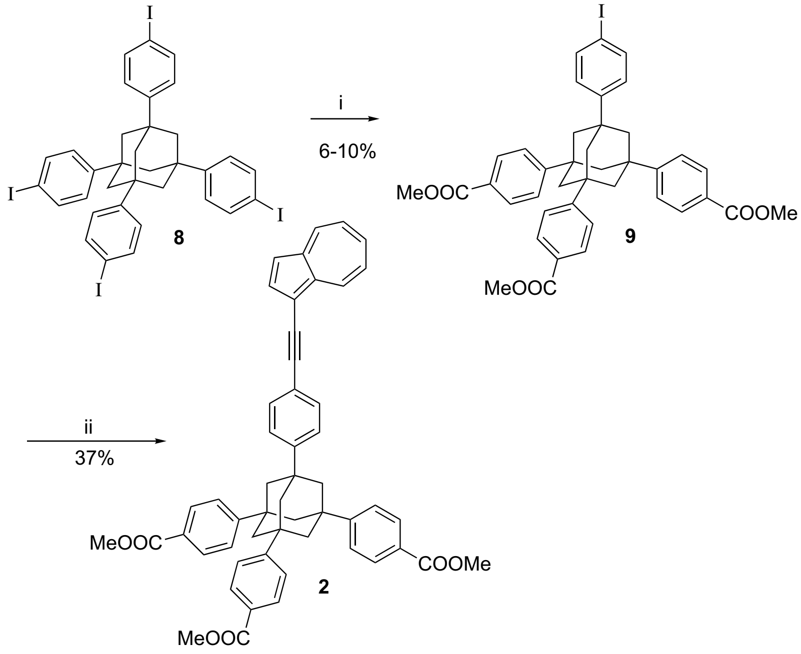


Figure 2. Absorption spectra of MeOH solutions of **1-COOH** (black solid line)and **1-COOH**/colloidal TiO_2 in EtOH (red dotted line). The spectra are overlayed with the absorption of the TiO_2 colloidal solution in EtOH (green dashed line). An identical behavior was observed for **2-COOH**.



Scheme 4. Synthesis of azulene tripod **2**. Reagents and conditions: (i) (a) *t*-BuLi, (b) CO_2 (g), H^+, (c) CH_2N_2, (d) separation (silica gel, hexane/ethyl acetate 4:1, gradient elution); (ii) $Pd(dba)_2$, CuI, *i*-Pr_2NH, PPh_3, **7b**, toluene, 24 h at rt.

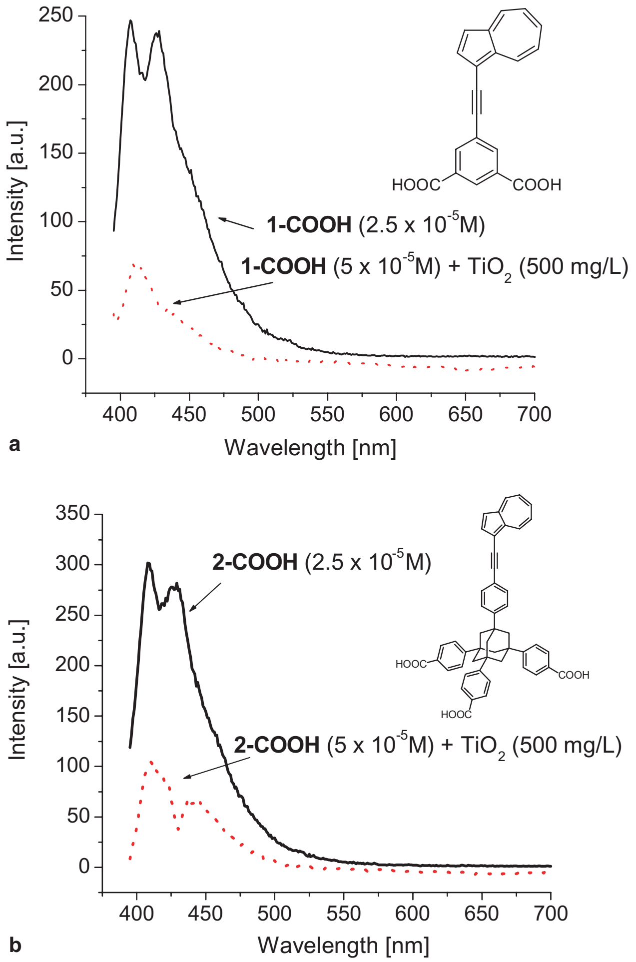


Figure 3. Fluorescence emission spectra of (a) **1-COOH** (black solid line) and **1-COOH**/colloidal TiO_2 (red dotted line). (b) **2-COOH** (black solid line) and **2-COOH**/colloidal TiO_2 (red dotted line). In all cases, the solvent was EtOH and $\lambda_{exc} = 382$ nm.

In conclusion two novel azulene chromophores, rigid-rod **1** and tripod **2**, have been synthesized and bound to colloidal solutions of TiO_2 nanoparticles. Steady-state and time-resolved fluorescence quenching studies are in progress.

Acknowledgments

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12. The synthesis of **9** has been reported: Wei, Q.; Galoppini, E. *Tetrahedron* **2004**, *60*, 8497. Compound **9** was contaminated by 1-phenyl-3,5,7-tris(4-carbomethoxyphenyl)adamantane, which was easily separated from **2** after the cross-coupling step. The yield of **9** is dependent on the reactions conditions as the solvent and the apparatus must be rigorously anhydrous.
13. Compound **1**: Mp 178–179 °C; IR 3021, 2195, 1726, 1439, 1396, 1344, 1249, 1215 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.69 (1H, d, $J = 10$ Hz), 8.61 (1H, s), 8.44 (2H, s), 8.34 (1H, d, $J = 9$ Hz), 8.05 (1H, d, $J = 4$ Hz), 7.71 (2H, t, $J = 10$ Hz), 7.37 (1H, dd, $J = 9, 6$ Hz), 7.29 (1H, t, $J = 10$ Hz), 3.99 (6H, s); ^{13}C NMR ($CDCl_3$) δ 166.0, 141.9, 141.8, 139.8, 139.1, 137.7, 136.6, 136.2, 131.1, 129.4, 125.6, 125.3, 124.7, 118.2, 109.8, 92.4, 88.4, 52.7; FAB-MS *m*/*z* 344 (M^+, 40); FAB-HRMS calcd for $C_{22}H_{16}O_4$ (M^+) 344.1049, found 344.1048. Compound **2**: Mp 142–144 °C; IR 3414, 2973, 2866, 1725, 1459, 1364, 1181, 1066 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.64 (1H, d, $J = 10$ Hz), 8.29 (1H, d, $J = 10$ Hz), 8.04 (6H, d, $J = 8$ Hz), 8.02 (1H, d, $J = 4$ Hz), 7.65 (1H, t, $J = 10$ Hz), 7.61 (2H, d, $J = 8$ Hz), 7.57 (6H, d, $J = 8$ Hz), 7.48 (2H, d, $J = 8$ Hz), 7.33 (1H, d, $J = 4$ Hz), 7.27 (1H, t, $J = 10$ Hz), 7.22 (1H, t, $J = 10$ Hz), 3.92 (9H, s), 2.21 (12H, 2s); ^{13}C NMR ($CDCl_3$) δ 166.9, 153.9, 148.1, 141.4, 141.2, 139.4, 138.7, 137.3, 136.4, 131.4, 129.8, 128.3, 125.1, 125.0, 124.6, 123.9, 122.3, 117.8, 110.6, 93.7, 85.9, 52.0, 46.7, 39.6, 39.4;

FAB-MS *m*/*z* 765 ($M+H^+$, 11); FAB-HRMS calcd for $C_{52}H_{45}O_6$ $(M+H)^+$ 765.3216, found 765.3213.

14. Methyl esters **1** and **2** were converted to the corresponding carboxylic acids **1-COOH** and **2-COOH** by standard basic hydrolysis (2 M KOH in MeOH, 12 h at rt).
15. The preparation of the colloidal solution employed in this work, that yielded TiO_2 particles about 15 nm diameter, is described in Ref. 4. For a review about the properties of the TiO_2 colloids, see: Kalyanasundaraman, K.; Gratzel, M. *Coord. Chem. Rev.* **1998**, *177*, 347. Given the large excess of the colloid and the very low (10^{-5} M) dye concentration it is estimated that the coverage is low, with a few to less than one chromophore per particle.