Supporting Information for:

Fluorescent Carbon by Covalently Attaching a BODIPY Fluorophore

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Experiment

Reagents

Potassium permanganate, tetrapropyl ammonium bromide (TPABr), hydroquinone, sodium carbonate, sodium bicarbonate, rhodamine B and activated carbon were purchased from Sigma Aldrich (St. Louis, MO). N-(6-aminohexyl)aminomethyl triethoxysilane (AHAMTES) was purchased from Gelest (Morrisville, PA). BODIPY FL-X succinimidyl ester was purchased from Invitrogen (Carlsbad, CA). Toluene, hydrochloric acid, methylene chloride, dimethylformamide (DMF), acetic acid and ethanol were purchased from Fisher Scientific.

Carbon surface hydroxylation. Carbon surface hydroxylation was performed using a literature procedure.[1] Activated carbon (60 ~ 100 nm) and Hypercarb (5 μm) were used. Typically 0.1 g of carbon particles and 100 mL of methylene chloride were added into a flask and sonicated for 10 min to disperse the carbon particles. Then 12.5 mL of $KMnO_4$ solution (0.25 g in H_2O/acetic acid,

2:3) and 0.12 g TPABr were added. The reaction mixture was stirred for 24 h at room temperature. The mixture was then washed with HCl and methanol. The solvent was removed by centrifugation and the hydroxylated carbon particles were dried under vacuum. The yield of the reaction is about 80%.

Silane coupling (vapor phase). AHAMETES is a silane-coupling reagent that can react with the hydroxyl groups. It has an amine group in the end of the alkyl chain that can react with BODIPY. The vapor phase reaction was conducted following a literature procedure.[2] About 1 mL of AHAMTES was added into a 10 mL flask. The hydroxylated carbon particles were added into a small vial (1.5 mL) and then the small vial containing the carbon particles was put into the flask containing the silane reagent (Fig. S-1). The liquid and carbon need to be separated completely to avoid solution phase reaction. Then the system was purged with Ar to remove water, and heated to 90 °C using for three days. The carbon particles were used for further modification without additional purification.

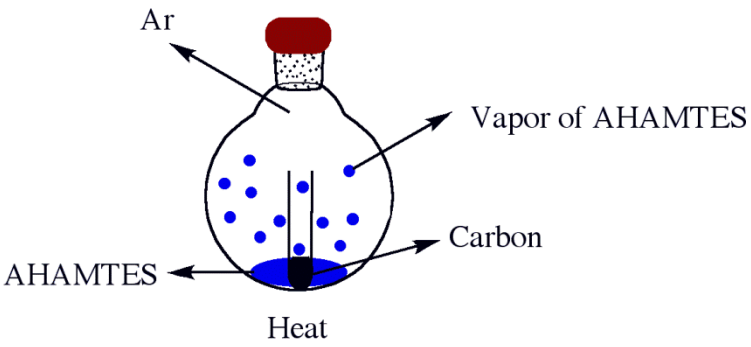

Figure S-1. Reaction setup of vapor phase silane coupling.

Silane coupling-solution phase.[3] *The hydroxylated carbon particles (50 mg) were dispersed in ethanol (50 mL) through sonication for 20 min. Then, 0.1 mL of AHAMTES was added. The reaction mixture was heated to reflux for 3 days. Then the particles were washed with ethanol to remove the unreacted AHAMTES. The particles were then dried in vacuum.*

BODIPY attachment. 50 mg of silanized carbon particles were dispersed in 0.5 mL of $NaHCO_3$ buffer solution (0.1 M, pH = 8.3). BODIPY (5 mg) was dissolved in DMF (0.5 mL). Then the BODIPY solution (50 μL) was mixed with the carbon suspension. The suspension mixture was agitated using a Dremel engraver (model 290-01) as a vortex device for 4 hours. The particles were washed with water and dichloromethane after reaction to remove the buffer salt and unattached BODIPY. The BODIPY attached carbon particles were dried in vacuum.

Measurement of fluorescence quantum yield. To determine the fluorescence quantum yield, Q, the integrated fluorescence intensity was plotted against the absorption at the excitation wavelength. The absorption intensity was measured using a CARY 5000 UV-Vis-NIR spectrometer (Varian). The fluorescence was measured using a CARY Eclipse Fluorescence spectrophotometer (Varian). The excitation wavelength used was 480 nm. Although the fluorescence intensity is higher at 485 nm, the left tail of the emission peak is blocked by the excitation light because the wavelengths of the emission and excitation are too close. Therrefore, 480 nm was used as the excitation wavelength. The slope, m, was obtained from the linear regression of the plot. A representative plot of Hypercarb is shown in Figure S-2. The fluorescence quantum yield was measured using the following equation:

$$Q = Q_R(m/m_R)(n^2/n_R^2), \qquad (2)$$

where n is the refractive index of the solvent and the subscript R refers to the reference sample. Rhodamine B in water was used as the reference. Its quantum yield is 31%.[4] Water is also used as the solvent for the fluorescent carbon particles. From the slope of the plot of integrated fluorescent intensity versus absorption, the fluorescence quantum yield of BODIPY modified Hypercarb and activated carbon was determined.

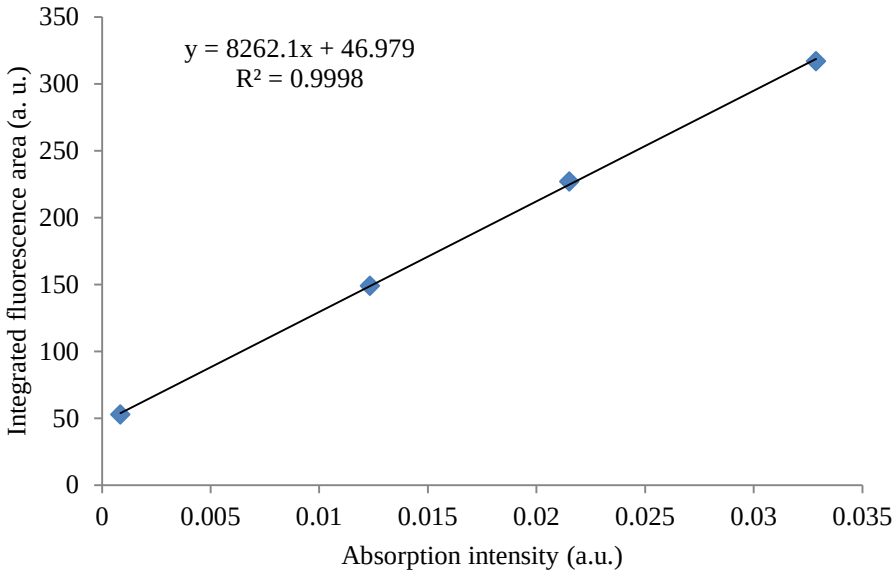

Figure S-2. Plot of integrated fluorescence area versus the absorption intensity of BODIPY modified Hypercarb.

References:

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[4] Magde, D.; Rojas, G. E.; Seybold, P. *Photochem. Photobiol.* **1999**, 70, 737.