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Electronic Supporting Information

Examining the Role of Acceptor Molecule Structure in Self-Assembled Bilayers: Surface Loading, Stability, Energy Transfer, and Upconverted Emission

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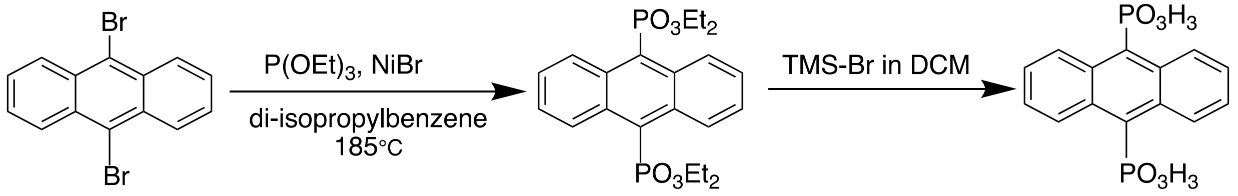
Materials and Methods:

a. Synthesis.

Anthracene-9,10-diphosphonic acid (**3**)



3a **3**

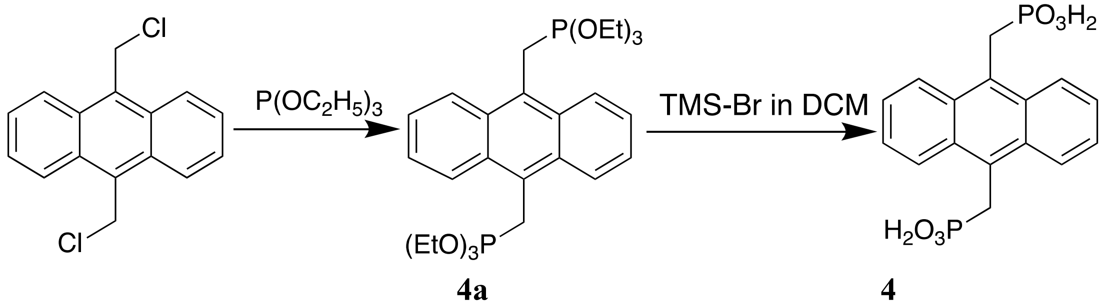
Tetraethyl anthracene-9,10-diylbis(phosphonate) (3a)

Synthesized following a reported procedure. [1] 9,10-dibromoanthracene (3.364 g, 10 mmol) is dissolved in 30 mL of 1,3-di-isopropylbenzene and heated to 150 °C under nitrogen. Nickel bromide (0.506 g, 3.6 mmol) is then added to this solution. The reaction mixture is raised to 185 °C followed by addition of triethylphosphite (8 mL, 50 mmol) directly into the solution dropwise over a period of 3 hr, then left heating for 20 hr. After cooling to room temperature, the solvent and the excess tritethylphosphite are distilled off at 40 °C. The product was extracted with hexane from the leftover solid and purified by column chromatography with a mixture of 70:30 chloroform to hexane. The product obtained from the column was recrystallized by dissolving it in dichloromethane and layering with hexanes to yield pure product. Yield – 1.23 g, 27%.

Anthracene-9,10-diylbis(phosphonic acid) (3)

3A (0.500 g, 1.1 mmol) is dissolved in 10 mL of 6 M HCl under nitrogen and heated at 110 °C for 20 hr. The off-white precipitate is collected, washed with water and dried in a vacuum desiccator to yield pure 3. Yield – 0.184 g, 49%. ESI-MS (m/z): Calculated for $C_{14}H_{12}O_6P_2$ – 338.2, Observed – 337.0 [M - 1]-; ^{1}H NMR (400 MHz, d_6-dmso) δ (ppm) 9.35 (s, 4H), 7.38 (s, 4H). ^{13}C spectrum could not be recorded due to poor solubility of the compound.

Anthracene-9,10-diylbis(methylene) diphosphonic acid (**4**)



4a **4**

Tetraethyl anthracene-9,10-diylbis(methylene)diphosphonate(4a)

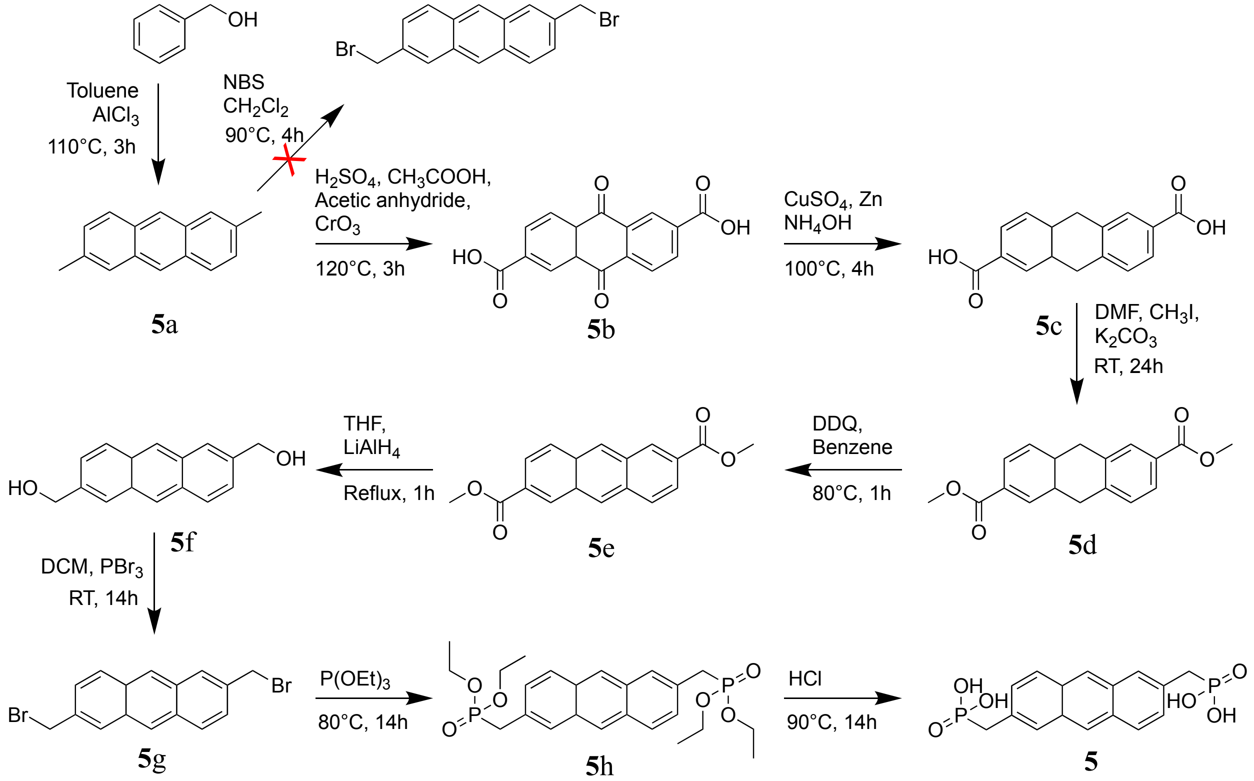
Synthesized following a reported procedure.[2] 9,10-bis(dichloromethyl)anthracene (0.449 g, 1.5 mmol) was dissolved in $P(OC_2H_5)_3$ (4 ml, 0.023 mol). The reaction mixture was heated to 150

°C in an oil bath and stirred for 18 h at this temperature under N_2 atmosphere. After being cooled to room temperature, the reaction mixture was poured into petroleum ether and filtered to give 0.526 g light yellow solid **4**A. Yield – 0.476 g, 75%.

Anthracene-9,10-diylbis(methylene) diphosphonic acid (4)

To a solution of 4A (0.526 g, 1.125 mmol) in 5 ml of dry dichloromethane under nitrogen, trimethylsilyl bromide (3 ml, 22.5 mmol) is added dropwise. The solution is then stirred at room temperature for 4 hours. After 4 hours, the reaction flask is placed in an ice bath and 10 ml of water is added while stirring. The bright yellow precipitate is collected, washed with water and dried in a vacuum desiccator to yield pure 4. Yield – 0.356 g, 86%. ESI-MS (m/z): Calculated for $C_{16}H_{16}O_6P_2$ – 366.2, Observed – 365.0 [M - 1]-; ^{1}H NMR (400 MHz, d_6-dmso) δ (ppm) 8.39 (dd, J = 6.8, 3.3 Hz, 4H), 7.51 (dd, J = 6.9, 3.2 Hz, 4H), 4.04 (d, J = 20.0 Hz, 4H). ^{13}C spectrum could not be recorded due to poor solubility of the compound.

2,6-anthracenediylbis(methylene)bisphosphonic acid (**5**)



2,6-Dimethylanthracene (5a)

Dry toluene (86 mL) was added to a flame dried 250 mL round bottom flask. Benzyl alcohol (1.04 mL) was added and stirred in an ice bath. $AlCl_3$ (16.9 g, 127.2 mmol) was added in small portions to prevent overheating. The reaction was refluxed at 110°C for 3 hours. The reaction was cooled and decomposed with ice, H_2O (36 mL) and concentrated HCl (23 mL). The solid was filtered and washed with H_2O (3 × 32 mL), EtOAc (3 × 14 mL), saturated $NaHCO_3$ (2 × 14 mL), and then H_2O (3 × 32 mL). The slurry was then vacuum filtered over a glass frit. The resulting solid was dried under vacuum at 80°C to yield **5**A, as a waxy yellow solid (5.68 g, 59.5% yield). ^{1}H NMR (400 MHz, *d_6*-chloroform) δ (ppm) 8.36 – 8.17 (m, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.73 (s, 2H), 7.28 (d, 2H), 2.54 (s, 6H).

2,6-Anthraquinonedicarboxylic acid (5b**)**

Concentrated sulfuric acid (0.29 mL), acetic anhydride (2.14 mL), and acetic acid (49.8 mL) were added to a 250 mL round bottom flask and stirred. CrO_3 (8.435g, 84.35 mmol) was added to the flask. The reaction was cooled in an ice bath and then **5**A (1.605 g, 7.669 mmol) was added slowly. The reaction was stirred for 2 hours in the ice bath. The reaction was then heated to reflux at 120°C until TLC indicated completion of the reaction ~3 hours and then cooled to room temperature. The reaction was poured into cold H_2O (300 mL), vacuum filtered, and washed with several portions of cold H_2O. The solid was dried under vacuum at 70°C to yield **5**B as a pale yellow solid (1.85 g, 81.5% yield). ^{1}H NMR (400 MHz, *d_6*-chloroform) δ (ppm) 8.69 (s, 2H), 8.42 (d, *J* = 8.0 Hz, 2H), 8.33 (d, *J* = 8.1 Hz, 2H).

9,10-Dihydroanthracene-2,6-dicarboxylic acid (5c**)**

$CuSO_4 \cdot 5H_2O$ (0.078 g, 0.312 mmol), Zn powder (5.716 g, 87.43 mmol), and NH_4OH (88 mL) was added to a 250 mL round bottom flask and stirred. The flask was placed in an ice bath and **5**B (1.85 g) was slowly added. The reaction was refluxed at 100°C while 44 mL of NH_4OH was added via addition funnel over 4 hours. Then it was cooled and filtered. The filtrate was acidified with 12 M HCl until a yellow solid precipitated. The solid was vacuum filtered and dried under vacuum at 70°C to yield **5**C as a bright yellow solid (1.614 g, 96.1% yield). ^{1}H NMR (400 MHz, *d_6*-chloroform) δ (ppm) 7.92 (s, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 4.06 (s, 4H).

Dimethyl 9,10-dihydroanthracene-2,6-dicarboxylate (5d**)**

In a flame dried 250 mL round bottom flask, DMF (30.9 mL), **5**C (0.642 g, 2.39 mmol), potassium carbonate (3.307 g, 23.9 mmol), and iodomethane (1.49 mL) was added and stirred for 24 hours under nitrogen. The reaction was added to 1 M HCl (120 mL). The precipitate was collected by vacuum filtration and then dried under vacuum at 70°C to yield a yellow solid (0.676 g, 95.3% yield). The solid was used without further purification.

2,6-dimethyl ester-2,6-anthracenedicarboxylic acid (5e**)**

DDQ (0.673 g, 2.97 mmol), **5**D (0.676 g, 2.281 mmol), and benzene (26 mL) were stirred in a 250 mL round bottom flask. The suspension was refluxed at 80°C for 1 hour under nitrogen and then cooled to room temperature. The reaction was vacuum filtered and washed with methanol. The solid was dissolved in minimal CH_2Cl_2 and loaded onto a silica gel column. The product was eluted with 25% EtOAc in hexanes. The fractions were evaporated to dryness to yield **5**E (0.582 g, 86.7% yield) as a yellow solid. ^{1}H NMR (400 MHz, *d_6*-chloroform) δ (ppm) 8.84 (s, 1H), 8.73 – 8.43 (m, 1H), 8.10 – 8.02 (m, 2H), 4.02 (s, 3H).

2,6-Bis(hydroxymethyl)anthracene (5f**)**

5E (0.582 g, 1.978 mmol) and dry THF (62 mL) was added to a 250 mL flame dried round bottom flask. The suspension was cooled in an ice bath. $LiAlH_4$ (0.173 g, 4.55 mmol) was added in several small portions with stirring. The reaction was stirred for 40 minutes at 0° C and then heated to reflux at 66° C for another hour. After cooling the reaction to room temperature, the reaction was quenched with EtOAc (40 mL). The solution was then poured over ice and 6 M HCl (150 mL) added. The aqueous layer was vacuum filtered while the organic layer was washed with brine, dried with sodium sulfate, and evaporated to dryness. The solids from the aqueous and organic layers were combined and dried under vacuum to yield **5**F (0.380 g, 80.7% yield) as a yellow solid. ^{1}H NMR (400 MHz, d_6-chloroform) δ (ppm) 8.49 (d, *J* = 6.8 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.95 (s, 1H), 7.44 (dd, *J* = 8.7, 1.5 Hz, 1H), 5.37 (t, *J* = 5.7 Hz, 1H), 4.69 (d, *J* = 5.4 Hz, 2H).

2,6-Bis(bromomethyl)anthracene (5g**)**

5F (0.541 g, 2.27 mmol) was added to dry DCM (87 mL) in a 250 mL flame dried flask. The suspension was cooled to 0° C in an ice bath. A solution of PBr_3 (0.108 mL) in dry DCM (9 mL) was added dropwise to the reaction mixture with stirring. After 15 minutes, the reaction was warmed to room temperature and stirred overnight. The reaction mixture was washed with 1 M NaOH (270 mL) and extracted with DCM (3 x 108 mL). The organic layers were then washed with 1 M HCl (270 mL) and extracted with DCM (3 x 81 mL) Finally the organic layers were washed with H_2O (135 mL) then brine (135 mL). The resulting solution was dried with sodium sulfate, filtered, and evaporated to dryness. The solid was dissolved in minimal DCM and loaded onto a silica gel column. The product was eluted with 30% DCM in hexanes. The fractions were combined and evaporated to dryness to yield **5**G (0.440 g, 53.3% yield) as an off yellow solid. ^{1}H NMR (400 MHz, d_6-chloroform) δ (ppm) 8.39 – 8.33 (m, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.97 (s, 1H), 7.50 (dd, *J* = 8.7, 1.7 Hz, 1H), 4.70 (s, 2H).

***P*,*P*'-[2,6-anthracenediylbis(methylene)]bis-*P*,*P*,*P*',*P*'-tetraethyl ester phosphonic acid (5**h**)**

1e (0.100 g, 0.275 mmol) and triethyl phosphite (2.27 mL) were added to a 50 mL round bottom flask and stirred. The reaction was refluxed at 160°C overnight. The reaction was vacuum distilled to remove triethyl phosphite. The product was purified on a silica column with 75% acetone in hexanes to remove impurities and then the solvent was changed to 10% MeOH/DCM. The fractions were combined and dried under vacuum to yield **5**H (0.089 g, 68.7% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, d_6-chloroform) δ (ppm) 8.38 – 8.24 (m, 2H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.86 (d, *J* = 3.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 4.13 – 3.91 (m, 8H), 3.33 (d, *J* = 21.9 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 12H).

***P*,*P*'-[2,6-anthracenediylbis(methylene)]bisphosphonic acid (5)**

1h was dissolved in HCl (35 mL) and added to a round bottom flask. The reaction was refluxed at 90°C overnight. The solution was cooled, washed with methanol, and evaporated to dryness. The solid was recrystallized from acetone and the precipitate was collected by vacuum filtration and washed with small portions of cold acetone. The solid was then dried under vacuum. The solid was further recrystallized by dissolving in minimal hot DMSO (at 60°C) followed by dropwise addition of CH_2Cl_2 until a precipitate formed. The precipitate was vacuum filtered and dried under vacuum to yield **5**I (0.038g, 55.2% yield) as a pale yellow solid. HRMS (ESI$^+$) m/z: Calculated for $C_{16}H_{16}NaO_6P_2$ ($[M+Na]^+$) – 389.03198, Observed – 389.03288. ^{1}H NMR (400 MHz, d_6-chloroform) δ (ppm) 8.61 – 8.28 (m, 2H), 7.97 (s, 2H), 7.86 (s, 2H), 7.42 (s, 2H), 3.15 (d, *J* = 22.1 Hz, 4H).

b. Analytical Methods.

^{1}H NMR spectra were recorded on a Bruker 400 MHz FT NMR (Model: Avance-DPX 600) and the spectral shifts are calibrated with respect to residual protonated solvent peaks (δ 7.26 and 2.49 for *d*$_6$-chloroform and *d*$_6$-dmso, respectively). ESI-MS measurements were carried out on a JEOL AccuTOF JMS-T100LC instrument.

Attenuated total reflectance infrared (ATR-IR) spectra were recorded using a Bruker Alpha FTIR spectrometer (SiC Glowbar source, DTGS detector) with a Platinum ATR quickSnap sampling module (single reflection diamond crystal). Spectra were obtained by placing dry, derivatized ZrO_2 slides active side down on the diamond face and data was acquired from 800 to 1800 cm^{-1} at a resolution of 4 cm^{-1}. All ATR-IR spectra are reported in absorbance with a blank versus atmosphere.

c. Center-to-center distance calculation

Molecular molar extinction coefficient of **A** in 0.1M KOH solution was measured. [Table S1]. 1 cm × 1 cm ZrO_2–**A** films was soaked in 3 mL of 0.1M KOH solution for 1 hour to dissolve **A** from the film. ZrO_2–**A** absorption before and after KOH treatment was measured [Table S1], lack of absorption of the latter sample indicates nearly all **A** were dissolved in the base solution. The absorbance of **A** in base solution was measured and the number of acceptor molecule, n, was calculated by $n=3\times10^{-3}A/(N_A\times \varepsilon\times b)$, where A is the absorbance, N_A is the Avogadro's number, b is the length of the cuvette which is 1 cm. Assuming acceptors were hexagonally packed on the ZrO_2 surface, each molecule should occupy$\sqrt{3}/4\times d^2_{A\text{-}A}$ surface area. By $A_{1\times1}=\sqrt{3}/4\times d^2_{A\text{-}A}\times n$, $d_{A\text{-}A}$ for each **A** was calculated.

Table S1 Absorption peak and extinction efficient of **A** in 0.1 M KOH

A in 0.1M KOH	1	2	3	4	5
λ_{abs} (nm) (ε, ×10^4 M^{-1} cm^{-1})	376 (0.99)	376 (1.19)	384 (0.88)	390 (1.09)	366 (0.39)
Absorbance	0.485	0.453	0.124	0.316	0.176

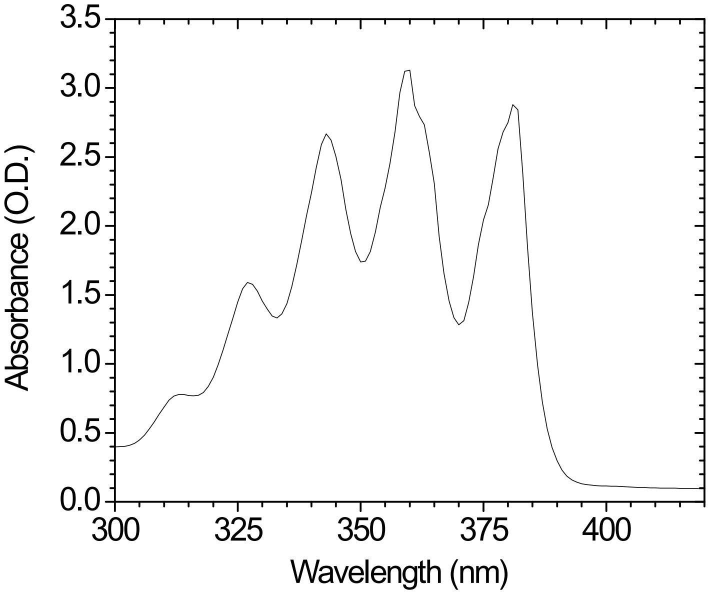


Figure S1. Absorption spectrum for anthracene in DMSO.

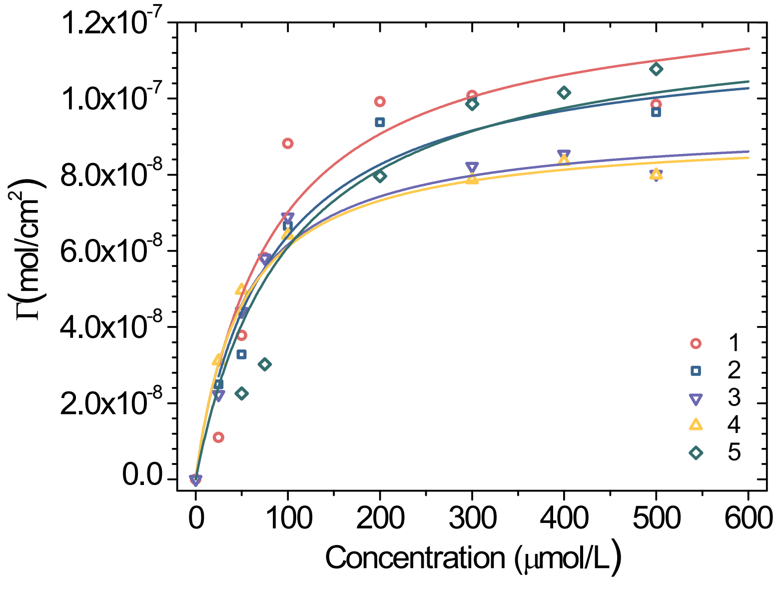


Figure S2. Surface coverage for ZrO_2-**A** films with respect to the concentration of **A** in DMSO loading solution. Data were fit to the Langmuir isotherm model (solid lines).

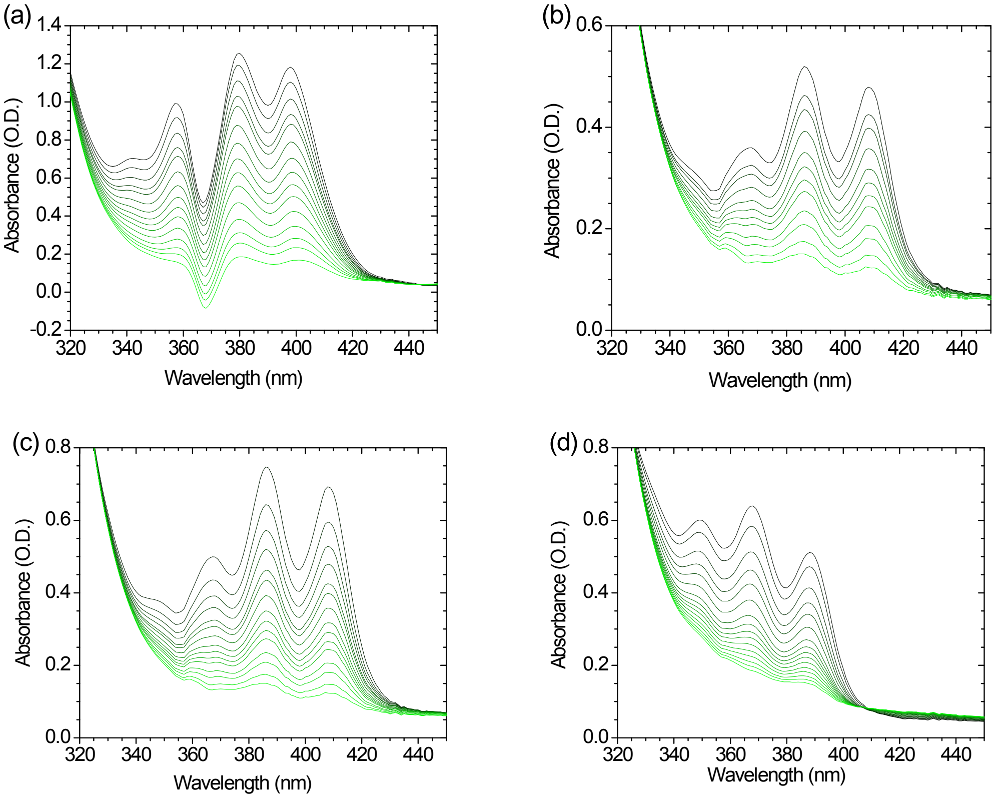


Figure S3. Changes in the absorption spectrum of ZrO_2-**A** where **A** is a) **2**, b) **3**, c) **4**, and d) **5** in MeCN under constant 365 nm (1.5 mW/cm^2) irradiation from 0 (black) to 2 hours (green)

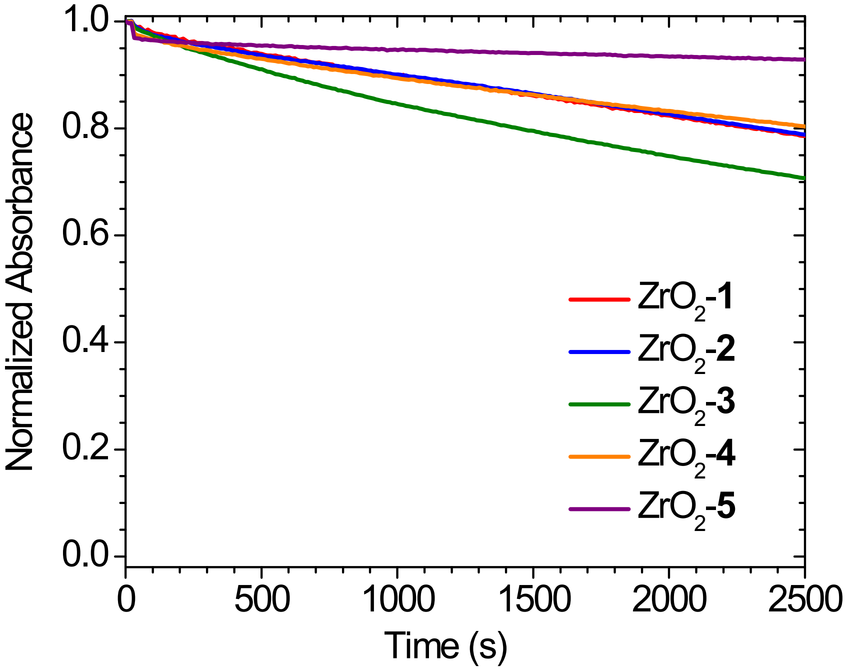


Figure S4. Changes in the absorption at absorbance maximum versus time for **1**-**5** on ZrO_2 in deaerated MeCN under constant 365 nm (1.5 mW/cm^2) irradiation.

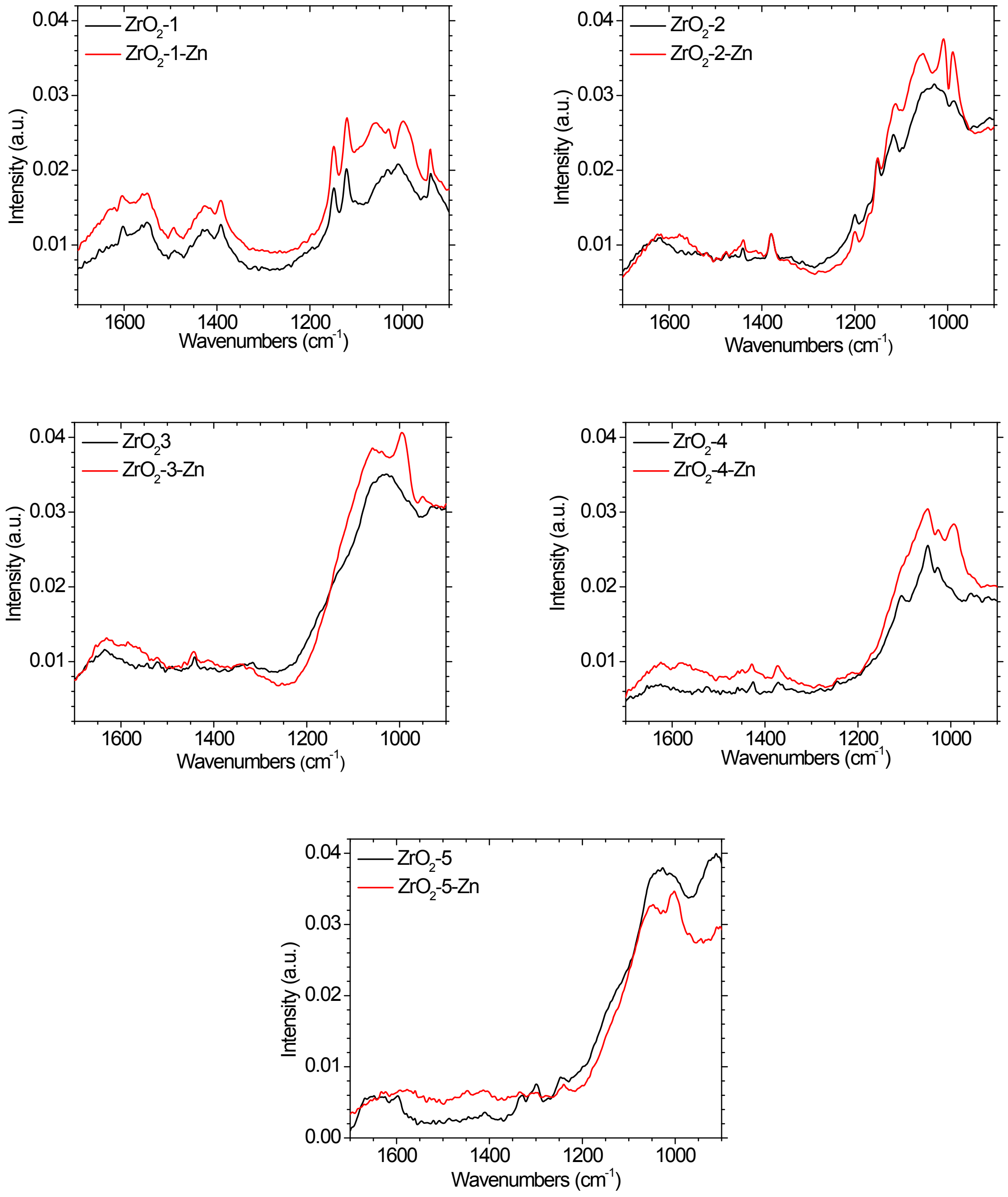


Figure S5. ATR-IR absorption spectra for ZrO$_2$-**A** before and after soaking in 400 μM Zn(CH$_3$COO)$_2$ in methanol.

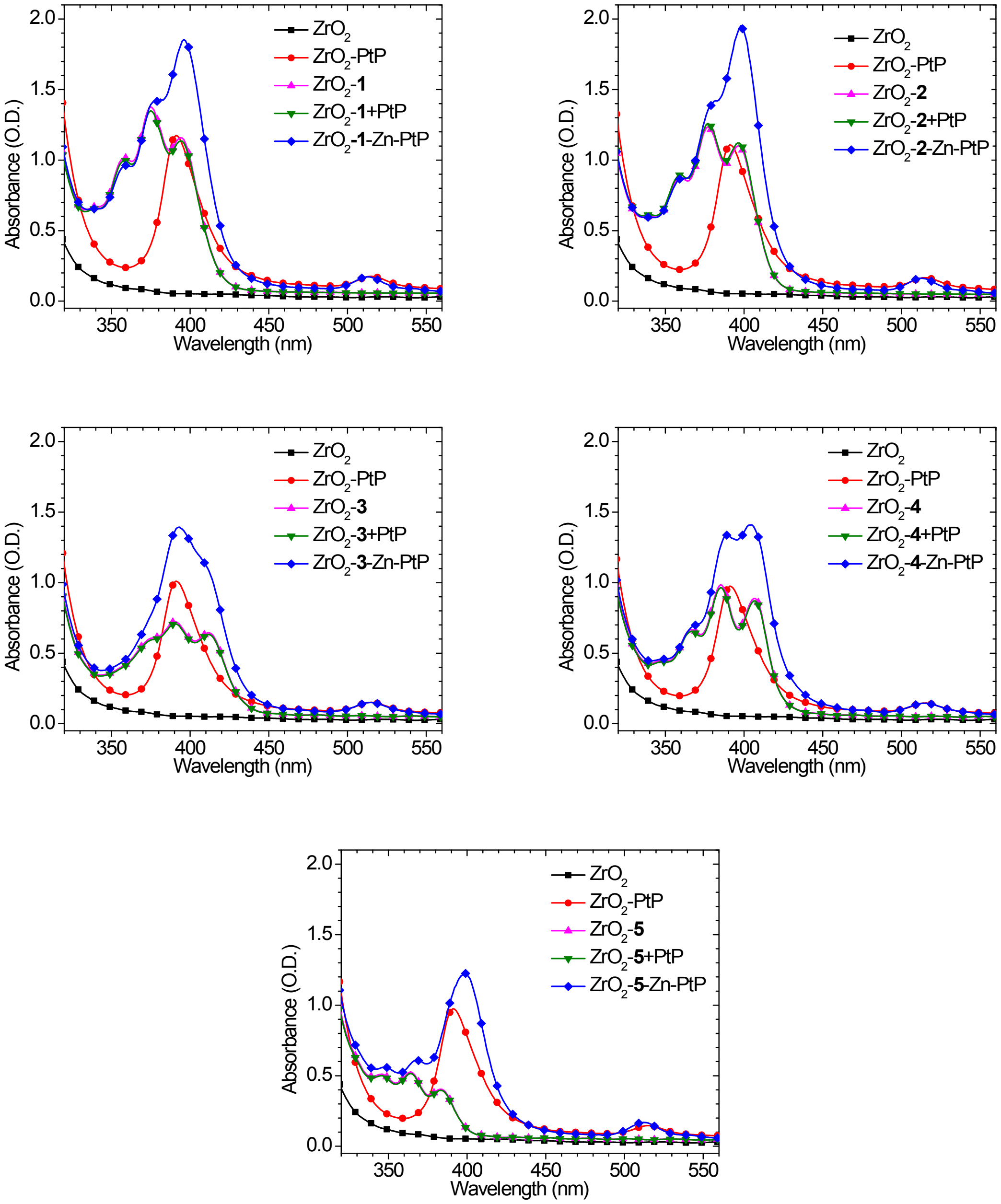


Figure S6. Absorption spectra for ZrO_2, ZrO_2-**A**, ZrO_2-**S** and ZrO_2-**A** after soaking in **S** with (ZrO_2-**A**-Zn-**S**) and without (ZrO_2-**A** + **S**) $Zn(CH_3COO)_2$ pretreatment. The **A** to **S** ratio in ZrO_2-**A**-Zn-**S** is ~10:1. **S** treatment time: 7 min, 6 min, 4 min, 4.5 min, 6 min for **1**~**5** respectively.

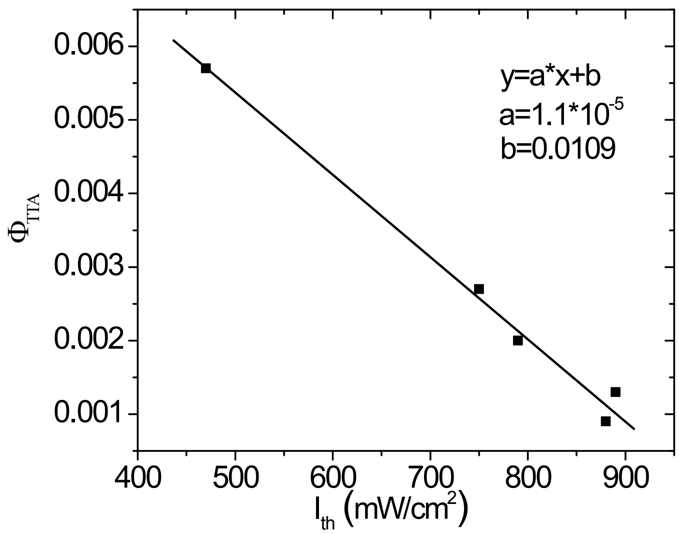


Figure S7. Φ_{TTA} versus I_{th} values.

1. M. Pramanik, N. Chatterjee, S. Das, K. D. Saha and A. Bhaumik, *Chemical Communications*, 2013, 49, 9461-9463.
2. Z. Jibo, X. Bin, C. Jinlong, M. Suqian, D. Yujie, W. Lijuan, L. Bao, Y. Ling and T. Wenjing, *Advanced Materials*, 2014, 26, 739-745.