Supplementary information

Light-Driven Molecular Shuttles Modified on Silicon Nanowires

Taiping Zhang,[a,b] Lixuan Mu,[a] Guangwei She,[a] Wensheng Shi*[a]

[a]*Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China ,100190*
[b]*Graduate University of Chinese Academy of Sciences, Beijing, China ,100039*
Email: a)shiws@mail.ipc.ac.cn.

4-Bromotoulene, 4-iodoaniline α-Cyclodextrin 4-Formyl benzene boronic acid and dansylamide were commercially available and used without further purification. ^{1}HNMR and ^{13}CNMR spectra were obtained on a Bruker Advance 400 NMR spectrometer using tetramethylsilane (TMS) as an internal reference. Fluorescence spectra were obtained with Hitachi F-4500 spectrophotometers (1-cm quartz cell used). The photoirradiation was carried on 18W light source of 365nm, 420nm, and 40W light source of 254nm, the distance between the lamp and the sample cell is 5cm. (When the photoirradiation was carried on 18W light source of 365nm, 420nm, and 40W light source of 254nm for 10 min, the fluorescence intensity of the S4-CD-SiNWs would reach the peak.)

Synthesis of the functional molecules

Synthesis of (4-bromomethyl-phenyl)-(4-iodo-phenyl)-diazene (S2) [1]:

2.5g (4-iodo-phenyl)-p-tolyl-diazene (S1, 7.8mmol)，1.45g NBS(8.1mmol)，0.1g BPO (0.4mmol) and 40mL CCl_4 were added in a round flask, the mixture was refluxed for 10h under nitrogen atmosphere. The reaction solution was cooled to room temperature and filtrated. The precipitate was repeatedly washed with ethanol and dried to afford red solid S2 (1.87g, 60%). ^{1}HNMR ($CDCl_3$): δ=4.55(s, 2H), δ=7.53(s, 2H), δ=7.64(d, 2H), δ=7.88(m, 4H)

Synthesis of *N, N*-2-((4-iodo-phenyl)-(4-methyl-phenyl)-diazene) dansylamide) (S3)

260mg S2 (0.65mmol), 96mg anhydrous potassium carbonate(1.3mmol), 107mg KI(1.3mmol), 244mg dansylamide(0.975mmol) and 40mL acetonitrile were added in a round flask and refluxed for 8h. The reaction solution was filtrated and washed with acetonitrile to give pure yellow solid (S3) (433mg,75%). 1H-NMR(d_6-DMSO): δ=2.82(s, 6H), δ=4.61(s, 4H), δ=7.23(d, 4H, J=8.36), δ=7.29(d, 1H, J=7.96), δ=7.56(m, 3H), δ=7.58(m, 6H), δ=7.60(s, 2H), δ=7.91(d, 3H, J=8.52), δ=8.20(d, 1H, J=7.16), δ=8.28(d, 1H, J=8.6), δ=8.47(d, 1H, J=8.6), m/z(MALDI-TOF): 890.6.

Synthesis of *N, N*-2-((4-formyl-biphenyl)-(4-methyl-phenyl)–diazene) dansylamide (S4)

100mg S3(0.175mmol), 4.9mg $Pd(PPh_3)_2Cl_2$, 1mg PPh_3, 48mg K_2CO_3(0.35mmol) and 26mg 4-formyl benzene boronic acid were dissolved in 3mL mixture of DMF and H_2O(v:v 5:1). The solution was stirred for 4h at 150□. The reaction solution was distilled under reduced pressure to afford red solid. The red solid was recrystallized with $CHCl_3$ and CH_3OH to give red solid S4 (43mg,45 %).^{1}H-NMR (400 MHz $CDCl_3$): δ=2.96(s, 6H), δ=4.52(s, 4H), δ=7.14(d, 4H), δ=7.63(t, 1H), δ=7.74(t, 1H), δ=7.77(m, 12H), δ=7.78(m, 9H), δ=8.00(d, 1H), δ=8.34(d, 1H), δ=8.36(m, 1H), ^{13}C-NMR($CDCl_3$): δ (ppm) 45.8, 50.0, 115.7, 123.2, 123.7, 127.9, 128.3, 128.5, 130.0, 130.2, 130.5, 130.9, 135.0, 135.8, 138.7, 142.3, 146.2, 152.3, 152.5. m/z(MALDI-TOF): 847.5.

Preparation of SiNWs

SiNWs were prepared by chemical vapor deposition of silicon monoxide powder. SiO powder (Aldrich, 99%) loaded in an alumina boat was located inside a high-temperature tube furnace. The system was vacuumized to 6 Pa. 95% Ar and 5% H_2 as carrier gas was introduced. The pump and gas current were accommodated to maintain the system pressure at 1×10^3Pa. Then the furnace was heated. The pump and gas current was closed when the temperature reached to 1200ºC. The system was further heated to 1350ºC and maintained for 6 hours, then the furnace was cooled to room temperature naturally.

The light yellow solid was obtained.

Modification of SiNWs

N*, *N-2-((4-formyl-biphenyl)-(4-methyl-phenyl)–diazene) dansylamide (S4,10mg) and APTES modified SiNWs (40mg) was stirred in DMF and water (5:1) at room temperature for 24 hours, then filtrated and the red solid was washed by DMF, water, dichloromethane and ethanol, red solid S4-SiNWs was obtained. S4 (10mg) and α-CD (20mg) were first dissolved in DMF and water (5:1) for 36 hours then the APTES modified SiNWs (40mg) was added. The reaction solution was also stirred at room temperature for 24h and then filtrated. The precipitate was repeatedly washed by DMF, water, dichloromethane and ethanol to obtain red solid S4-CD-SiNWs.

Reference

[1] D. H. Qu, Q. C. Wang, J. Ren, H. Tian, Org. Lett. 2004, 6, 2085-2088

Fig. S1 The structures of the functional molecules and the SiNW modification procedure.

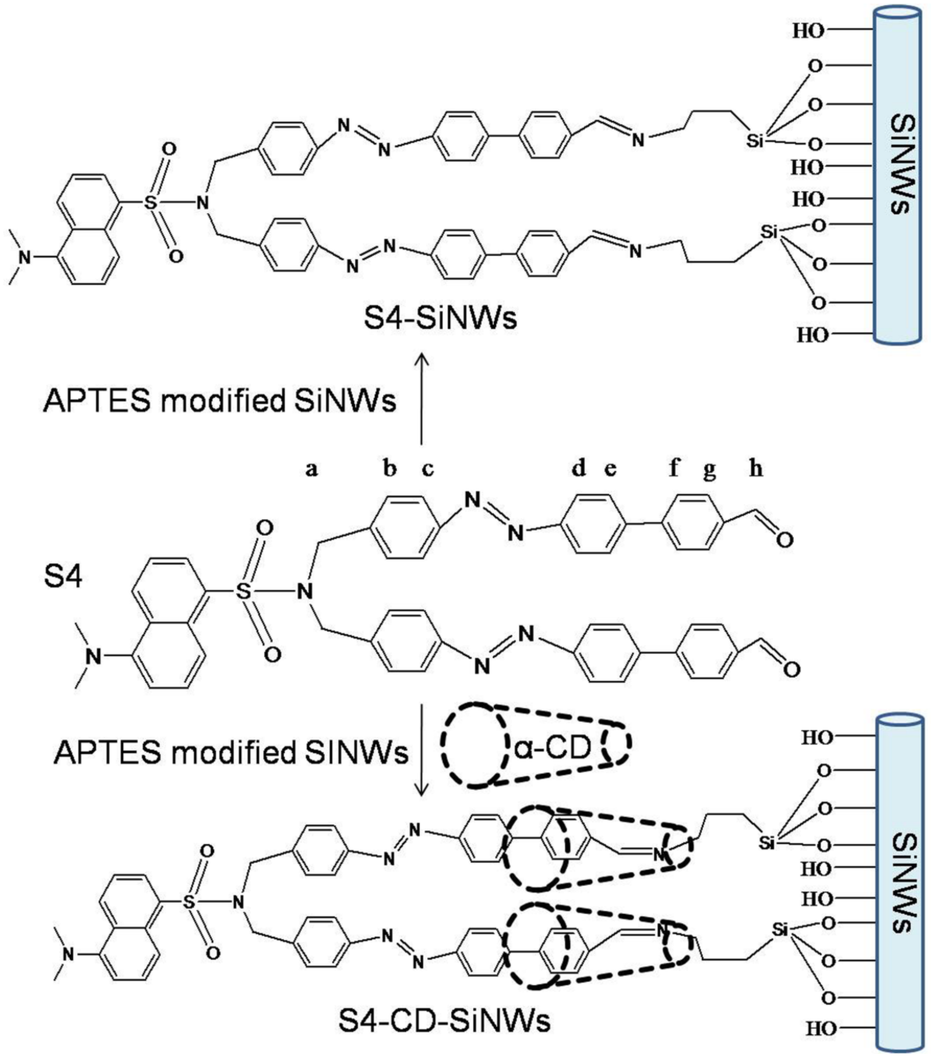


Fig. S2 the HRTEM image of SiNWs

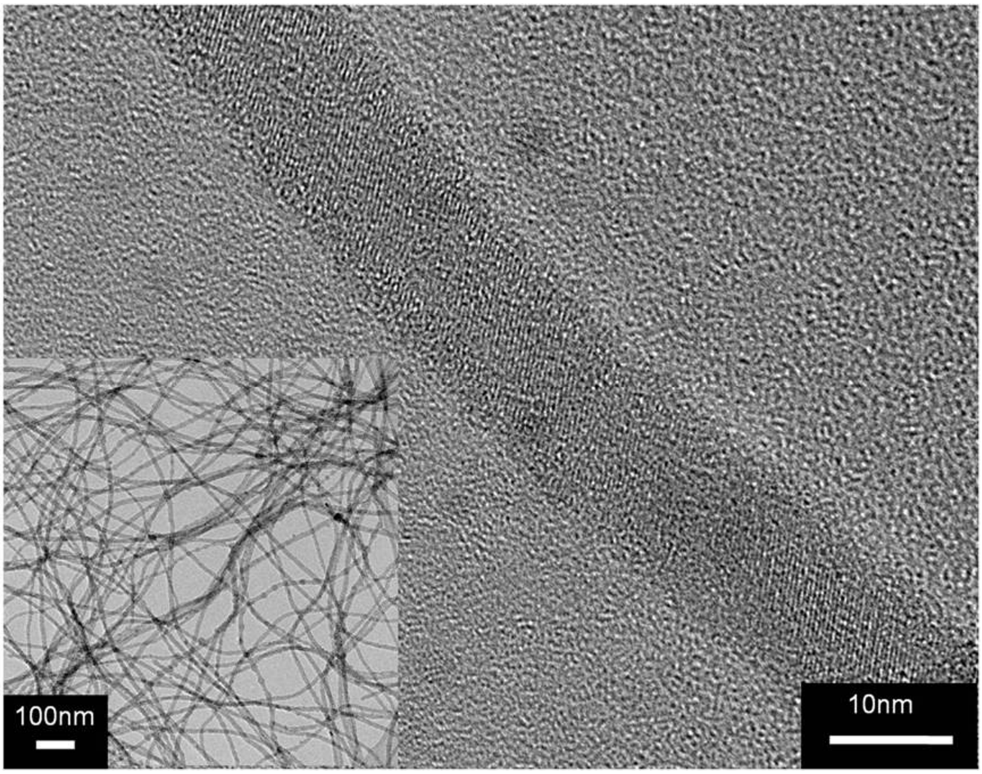
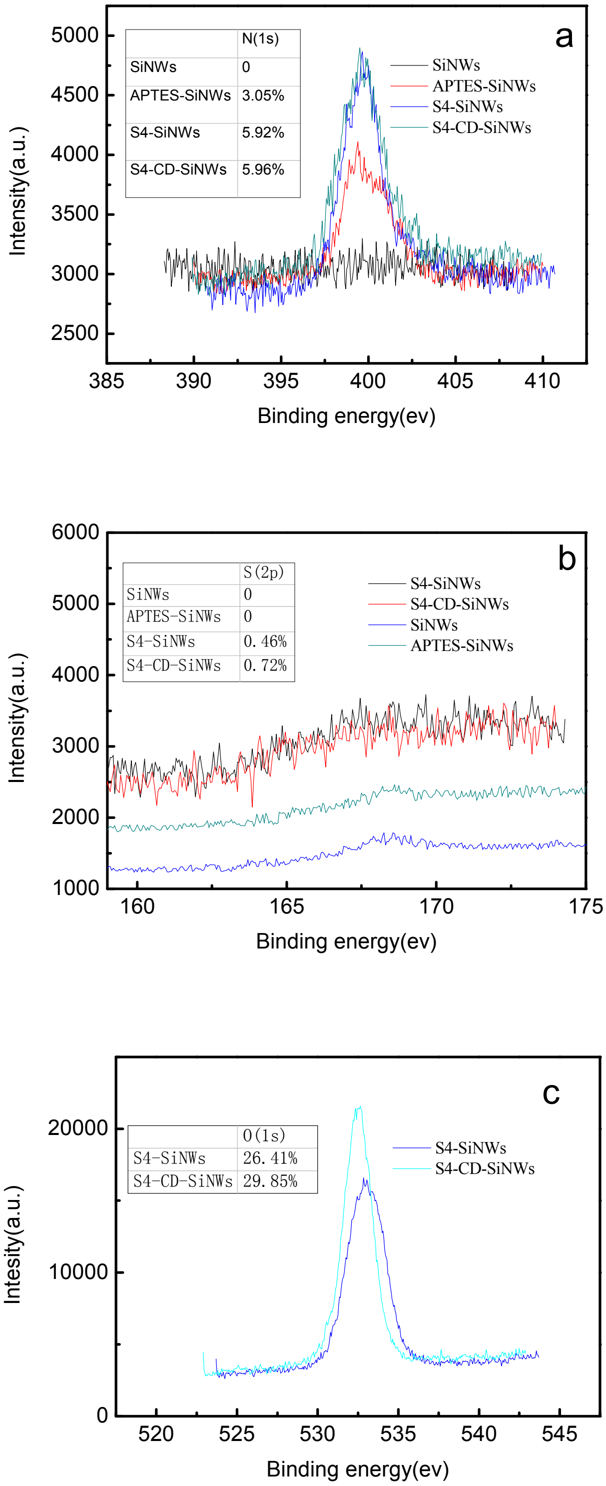


Fig. S3 The XPS spectra of SiNWs, APTES-SiNWs, S4-SiNWs and S4-α-CD-SiNWs. a) N (1s), b) S (2p), c) O (1s)



	N(1s)
SiNWs	0
APTES-SiNWs	3.05%
S4-SiNWs	5.92%
S4-CD-SiNWs	5.96%

	S(2p)
SiNWs	0
APTES-SiNWs	0
S4-SiNWs	0.46%
S4-CD-SiNWs	0.72%

	O(1s)
S4-SiNWs	26.41%
S4-CD-SiNWs	29.85%

Fig. S4 Infrared spectroscopy (IR) of APTES-SiNWs, S4-CD-SiNWs and S4

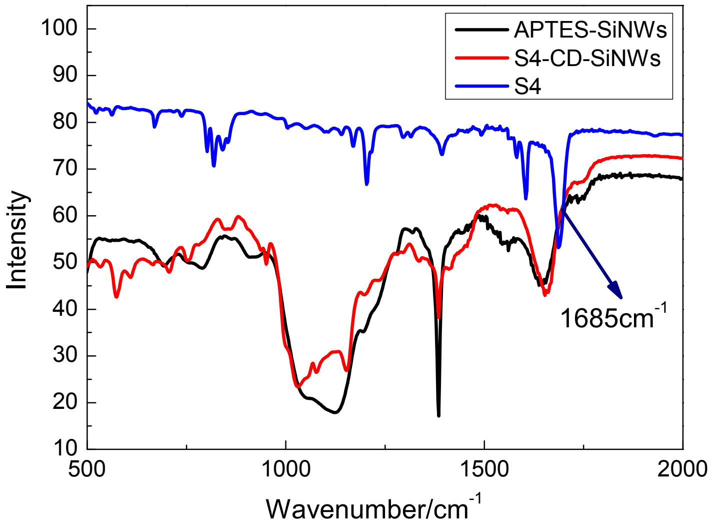
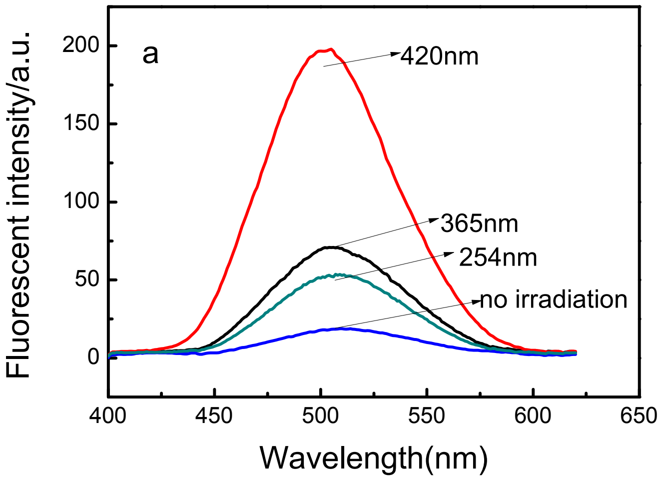


Fig. S5 a) Fluorescence spectra of S4-CD-SiNWs sequently irradiated with 254nm light and 420nm light, 365nm light b) Fluorescence spectra of S4-SiNWs independently irradiated with 254nm light and 420nm light, 365nm light.



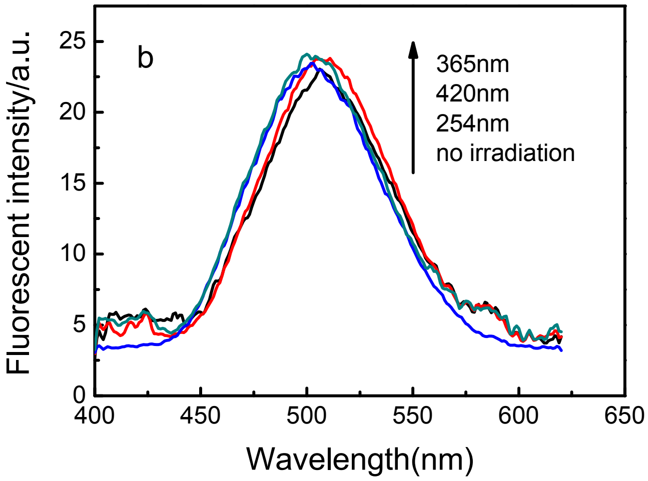


Fig. S6 Fluorescence intensity of S4-CD-SiNWs under irradiation of light at different wavelength with time

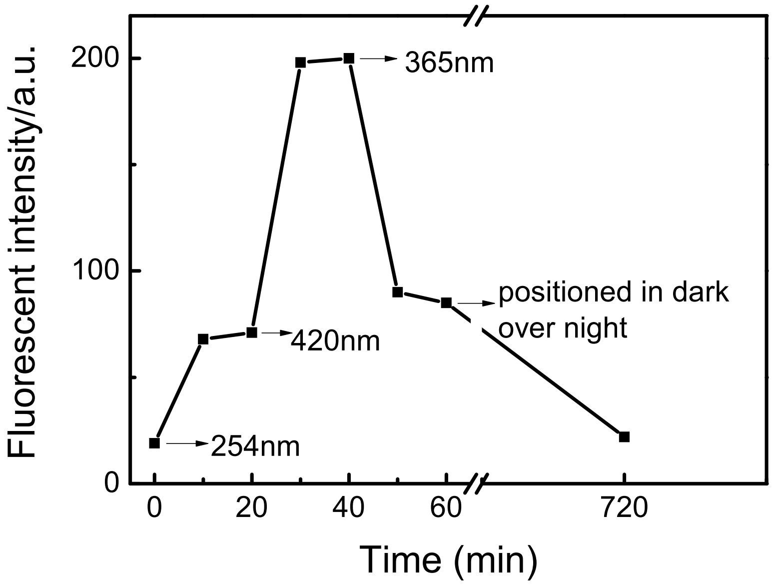


Fig. S7 ^{1}HNMR spectroscopy of a) S4，b) S4-CD，c) S4-CD system with 365nm light irradiation，d) S4-CD system c) irradiated by 420nm light. All ^{1}HNMR was performed in d-DMSO and $CDCl_3$.

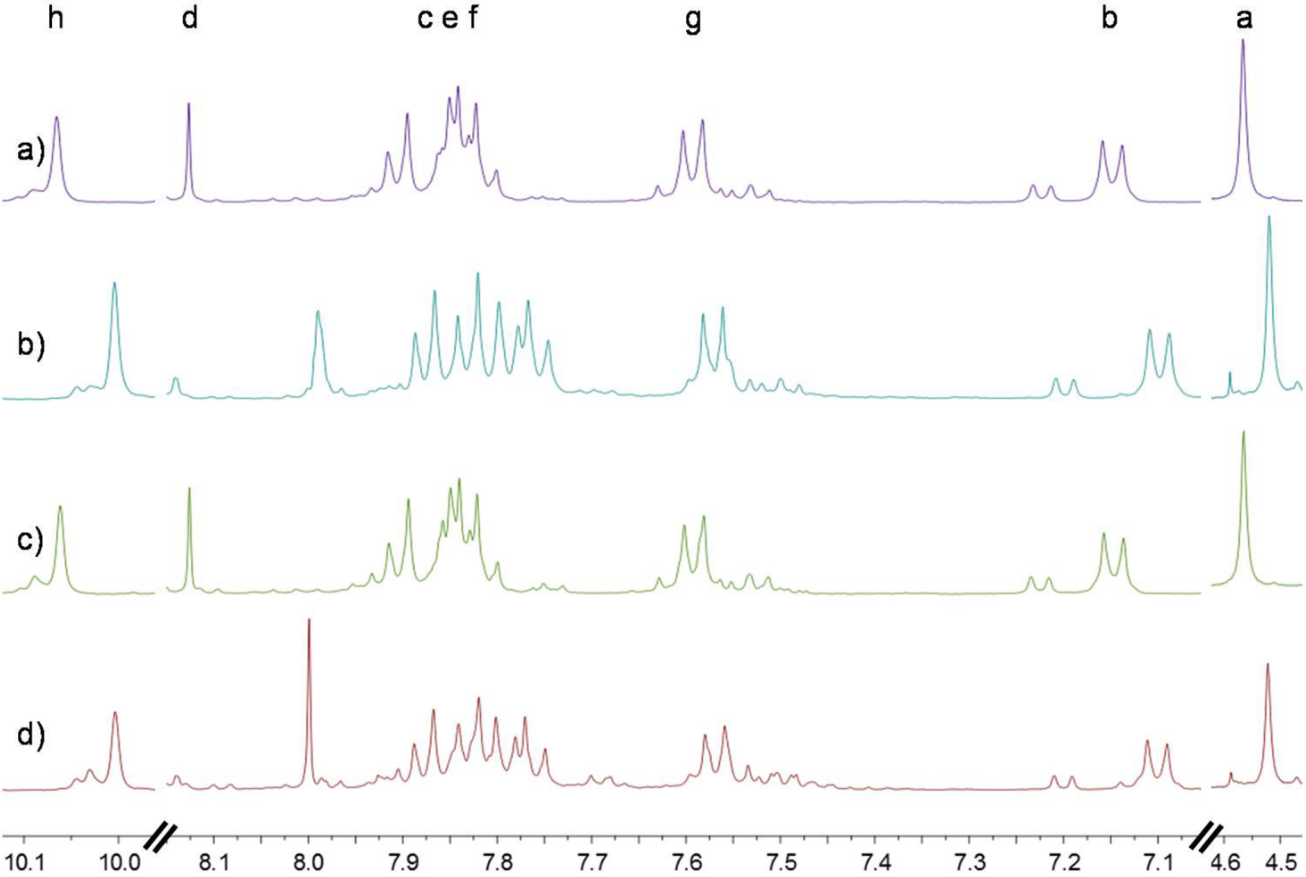


Fig. S8 Decay curve of fluorescence intensity of the S4-CD-SiNWs in the dark after 254 nm and 420 nm irradiation for 10min each. I_0 represents the peak fluorescence intensity after 254 nm and 420 nm irradiation for 10min each. I represents the fluorescence intensity after the sample was put in the dark as time decays.