

## Supplementary Data

**This work** presents the synthesis of a polysilane modified with azocrown macrocycle photoreceptors and its behavior during the UV induced photoisomerization.

### Experimental Procedure

Poly[diphenyl-co-methyl(H)]silane was synthesized by Wurtz reductive coupling of diphenyldichlorosilane with methyl(H)dichlorosilane in homogeneous system using Na/K alloy in the presence of 18C6 crown ether using the following procedure:

A reaction flask equipped with magnetical bar, condenser and dropping funnel, was charged with 30 cm<sup>3</sup> of a 0.2 mole/dm<sup>3</sup> THF solution of Na complex with 18C6 crown ether. Then, an equivalent amount of R<sub>2</sub>SiCl<sub>2</sub> (R= CH<sub>3</sub>; C<sub>6</sub>H<sub>5</sub>) and CH<sub>3</sub>HSiCl<sub>2</sub> mixture in a predetermined molar ratio was added at room temperature under continuous stirring in argon atmosphere, until discoloration of the blue metal solution. Next the reaction mixture was filtered and the solvent was distilled under vacuum. The remained solid product was solved in 5-10 ml of chloroform, reprecipitated in methanol then boiled in diethylether, filtered and vacuum-dried. Yield: polydiphenyl(H)silane (PSHDF)= 70 %.

(4-Hydroxyphenylazo)dibenzo-18-crown-6 was prepared in laboratory.

(C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub>) (480) Calcd: C 63.64, H 5.62, N 5.81; Found: C 64.9, H 5.87, N 5.83.

IR (KBr): 3300-3500 (O-H), 2880 and 2960 (CH<sub>2</sub>, CH<sub>3</sub>), 1600 and 1513 and 1453 (C=C), 1260 and 1120 (C-O) cm<sup>-1</sup>.

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ= 3.9 - 4.1(d, H<sup>6,7</sup>), 6.70 - 6.85, (d, H<sup>11</sup>), 7.03 (s, H<sup>13</sup>); 7.27 (s, H<sup>8</sup>); 7.32 - 7.42 (d, H<sup>9</sup>) 7.50 - 7.65 (d, H<sup>10</sup>) (assignment in Scheme 1).

### Synthesis of poly[diphenyl-co-methyl(bromopropyl)]silane (PSBDF).

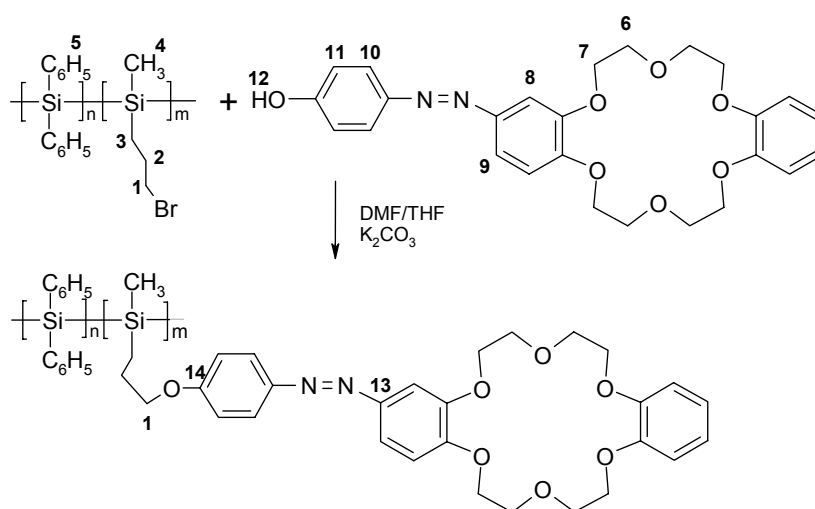
4 g (10 mmol) Poly[diphenyl-co-methyl(H)]silane were dissolved in 20 ml freshly distilled toluene with 0.2 ml solution 1% of hexachloroplatinic acid in isopropanol. The reaction mixture was heated at 80 °C and 1.12 g (10 mmol) allyl bromide was added dropwise. When the addition was complete, the reaction mixture was maintained 120 h under stirring at the prescribed temperature. Finally the unreacted allyl bromide and solvent were distilled at 10 mm Hg and 70 °C. The resulted product, a viscous liquid, was analyzed to establish the content in bromopropyl groups. Yield: 3.6 g (η= 68%). IR (KBr): 3080 (Car-H), 2980 (C- H), 2150 (Si-H), 1600 and 1513 and 1458 (Car-Car), 805 and 1265 (Si-CH<sub>3</sub>), 470 and 1070 (Si-Si), 520 (C- Br) cm<sup>-1</sup>.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 0.15 (d,  $-\text{SiCH}_3$ ), 0.78 (m,  $-\text{SiCH}_2-$ ), 1.73 (m,  $-\text{CH}_2-$ ), 3.31 (m,  $-\text{CH}_2\text{Br}$ ), 4.21 (s, Si-H), 7.25 (m,  $-\text{SiC}_6\text{H}_5$ ).

Yield (bromopropyl): 91% ( $^1\text{H-NMR}$ ).

### Synthesis of poly[diphenyl-co-methyl(propyl-oxyphenylazo-dibenzo-18C6)]silane (PSADF) (Scheme 1).

2.4 g (4.5 mmol) Bromopropyl- polysilane were dissolved in 30 ml DMF and 1.8 g (3.9 mmol) (4-hydroxyphenylazo)dibenzo-18C6 and 0.7 g anhydrous  $\text{K}_2\text{CO}_3$  were added. The reaction mixture was maintained under stirring at  $80\text{ }^\circ\text{C}$  for 26 h then cooled to room temperature and  $\text{K}_2\text{CO}_3$  was filtered. The azocrown polysilane was obtained by precipitating in 500 ml HCl sol. 0.1N, filtering and washing to neutral pH. Finally the resulted solid was washed three times with solvent tetrahydrofuran (THF) to eliminate the unreacted polysilane. Yield: 2.1 g ( $\eta$ = 63%) of brown solid powder.  $\text{Mp}$ =  $232\text{ }^\circ\text{C}$ .



**Scheme S1.** Synthesis of azocrown polysilane.

IR (KBr): 3300-3500 (OH), 2880 and 3080 (C-H), 1458 and 1513 and 1600 (C-Car), 1130 and 1260 (C - O), 1050 (Si-Ph), 804 and 1260 (Si- $\text{CH}_3$ )  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 0.15 ( $\text{H}^4$ ), 0.62 ( $\text{H}^3$ ), 1.46 ( $\text{H}^2$ ), 3.80-4.15 ( $\text{H}^{1,6,7}$ ), 6.81-7.80 (H, aromatic) (Figure 1).

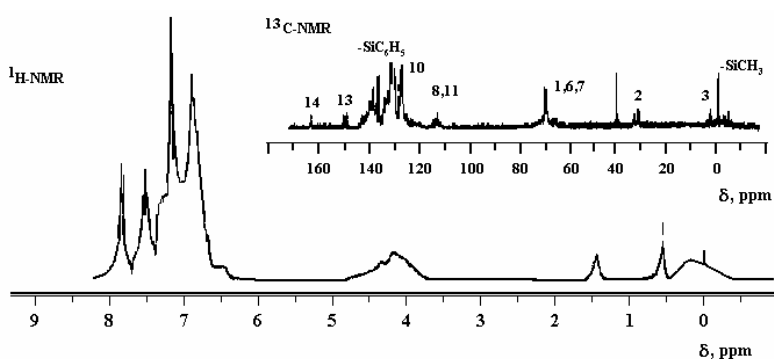
$^{13}\text{C-NMR}$  (DMSO):  $\delta$  = -5.2 ( $-\text{C}^4$ -), -0.9 ( $-\text{C}^4$ ), 4.2 ( $\text{C}^3$ ), 30.2 ( $\text{C}^2$ ), 67.9 ( $\text{C}^{1,6,7}$ ), 110.4 ( $\text{C}^{8,11}$ ), 127.3 ( $\text{C}^{10}$ ), 132.1-135.3 ( $-\text{SiC}_6\text{H}_5$ ), 148.2-153.1 ( $\text{C}^{13}$ ), 163.1-165.2 ( $\text{C}^{14}$ ) (Figure 1).

TGA analysis showed 2 thermal decomposition steps: 260- 400 °C with the maximum rate of mass loss at 290 °C; 400- 750 °C with the maximum rate of mass loss at 485 °C.

DSC analysis in inert gas showed an endothermic peak around 232 °C corresponding to the melting point of the polymer.

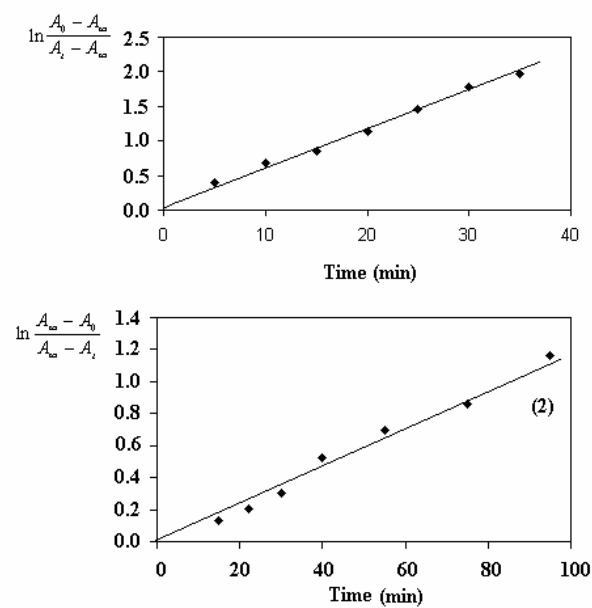
UV-VIS (DMSO):  $\lambda_{\max}(\epsilon)$ = 280 (13812); 332 (18137); 480 (5658)

UV Irradiation: 10 mg/ml polymer solutions in DMSO were irradiated in a standard spectrophotometer quartz cuvette with light from a high-pressure 350 W Hg arc lamp. UV irradiation was achieved by the use of a 404.7(2) nm UV bandpass filter (Andover) and an exposure energy irradiation of aprox. 6 mW/ cm<sup>2</sup>.



**Figure S1.** <sup>1</sup>H- and <sup>13</sup>C- NMR spectra of azocrown polysilane.

Thermal recovery was obtained by gentle heating of samples at 70 °C and measurement of the UV absorption band intensity at pre-determined intervals of time.



**Figure S2.** (1) First order plot for trans-cis photoisomerization of azocrown polysilane;  
(2) First order plot for cis- trans thermal recovery of azocrown polysilane.