

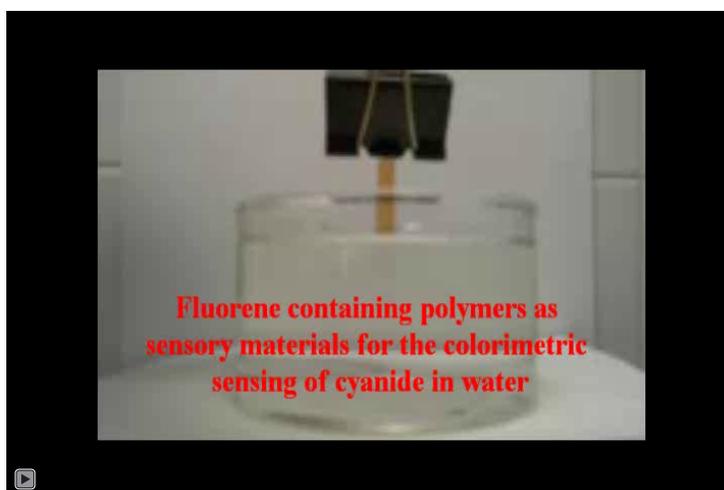
## SUPPLEMENTARY INFORMATION

### Putting to work organic sensing molecules in aqueous media: fluorene-derivative containing polymers as sensory materials for the colorimetric sensing of cyanide in water.

Saúl Vallejos, Pedro Estévez, Félix C. García, Felipe Serna, José L. de la Peña, José M. García.\*  
*Departamento de Química, Facultad de Ciencias, Universidad de Burgos. Plaza de Misael Banuelos s/n, E-09001 Burgos, Spain*

#### S0. Real-time movie showing the colorimetric response of a film 4 toward cyanide anions in aqueous media

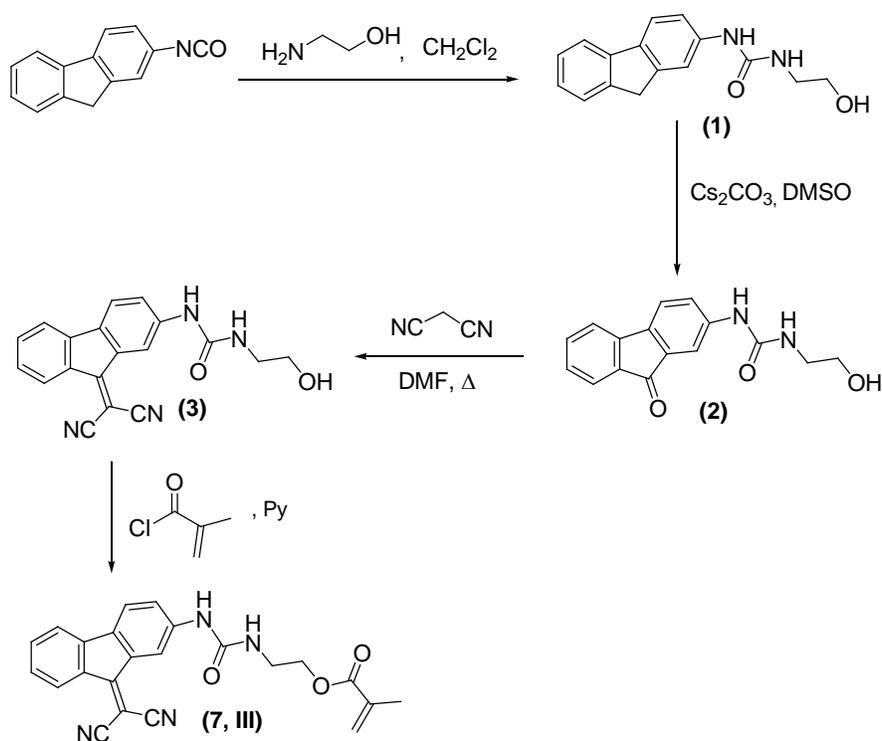
This paper describes a strategy followed to achieve a sensing phenomenon in aqueous media using water-insoluble organic molecules. Thus, we have prepared a methacrylamide and a methacrylate with pendant cyanide chemosensors based on a fluorene-derivative motif, and we have fabricated highly hydrophilic membranes by means of copolymerizing these hydrophobic monomers with others. Therefore, upon absorption of water in the membranes, solvated ions enter the membrane by a simple diffusion mechanism reaching the hydrophobic chemosensor motifs, giving rise to the macroscopic sensing phenomenon. In this way, we have prepared solid materials (dense membranes or films) capable of selectively detecting cyanide, with an extremely low detection threshold, in aqueous solution by means of color changes (naked-eye sensing) (13 ppb).



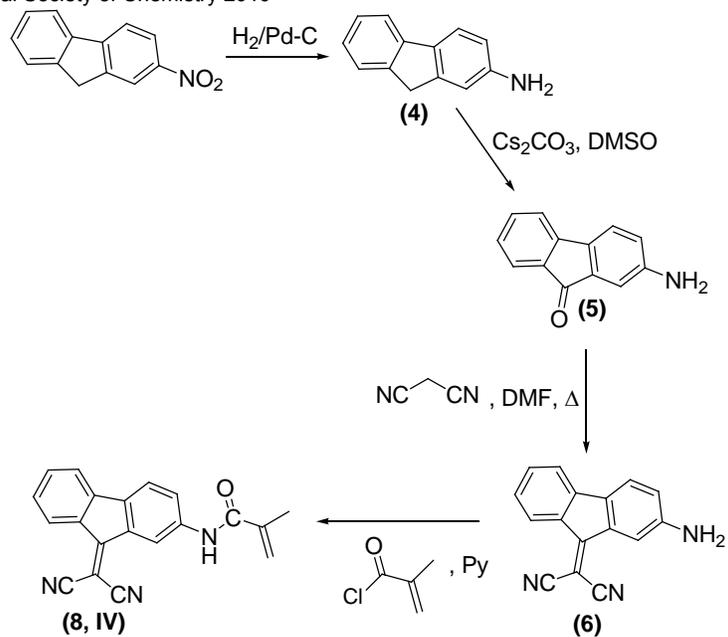
All materials and solvents were commercially available and used as received, unless otherwise indicated including the following: sodium cyanide (Panreac, 98%), 2-Ethoxyethyl methacrylate (Aldrich, 99%), 2-isocyanato-9H-fluorene (Aldrich, 98%), ethanolamine (Merck, 98%), cesium carbonate (Aldrich, 99%), malononitrile (Aldrich, 99%), 2-nitro-9H-fluorene (Aldrich, 98%), Pd/C (Aldrich, 10%), methacryloyl chloride (Fluka, 97%), 2-(2-aminoethoxyethanol) (Aldrich, 98%), fluorenone (Aldrich, 98%), ethylene glycol dimethacrylate (Aldrich, 98%), DMSO (Merck, 99%), acetone (Aldrich, 99%), ethanol (Aldrich, 99%), dichloromethane (Aldrich, 99%), DMF (Aldrich, 99%), hexanes (Aldrich, 99%), and ethyl acetate (Aldrich, 99%). Pyridine was dried under reflux over sodium hydroxide for 24 h and was distilled over 4Å molecular sieves. Azo-bis-isobutyronitrile (AIBN, Aldrich, 99%) was recrystallized twice from methanol.

## S2. Synthesis of intermediates, monomers and model

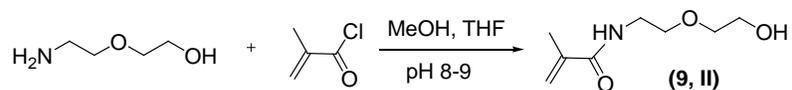
The overall monomer synthetic steps are shown in Schemes S1 to S4. The structure of the intermediates and monomers were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (nuclear magnetic resonance) and by FT-IR (infrared spectroscopy). The spectra showed that the products were high purity chemicals.



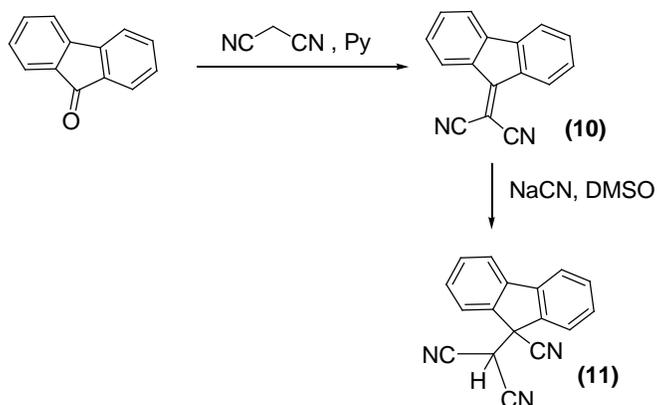
**Scheme S1.** Synthesis of the monomer 2-(3-(9-(dicyanomethylene)-9H-fluoren-7-yl)ureido)ethyl methacrylate



**Scheme S2.** Synthesis of the monomer N-(9-(dicyanomethylene)-9H-fluoren-7-yl)methacrylamide



**Scheme S3.** Synthesis of the monomer N-[2-(2-hydroxyethoxy)ethyl]methacrylamide

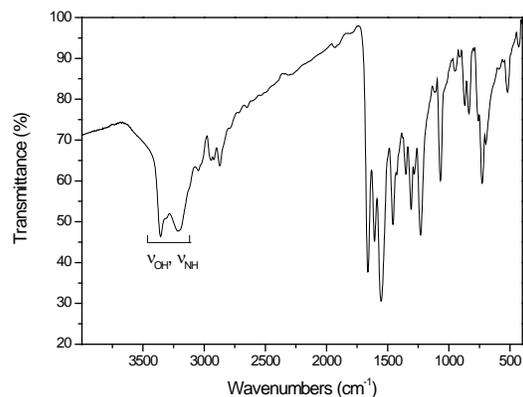
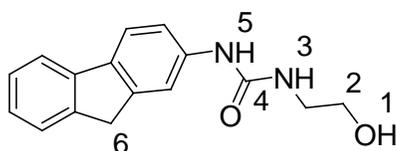


**Scheme S4.** Synthesis of the model 9-(dicyanomethyl)-9H-fluorene-9-carbonitrile

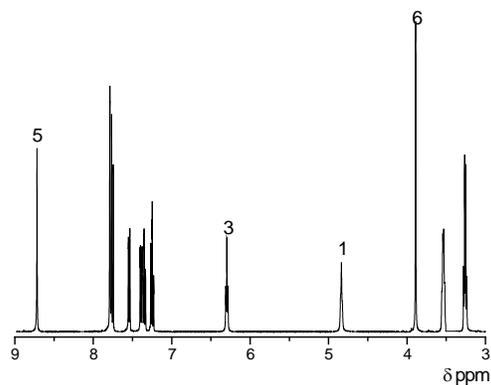
### Synthesis of 1-(9H-fluoren-7-yl)-3-(2-hydroxyethyl)urea (**1**)

To a 500 mL flask fitted with a mechanical stirrer was added 25 mmol of 2-isocyanato-9H-fluorene and 50 mL of dichloromethane. Subsequently, 25 mmol of ethanolamine was added dropwise, and the solution was stirred at 0 °C for 30 min and then at rt for 6 h. Finally, the product 1-(9H-fluoren-7-yl)-3-(2-hydroxyethyl)urea was filtered off and washed with dichloromethane. Yield: 96%.

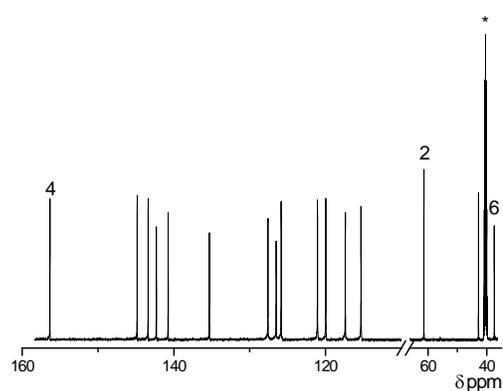
a)



b)

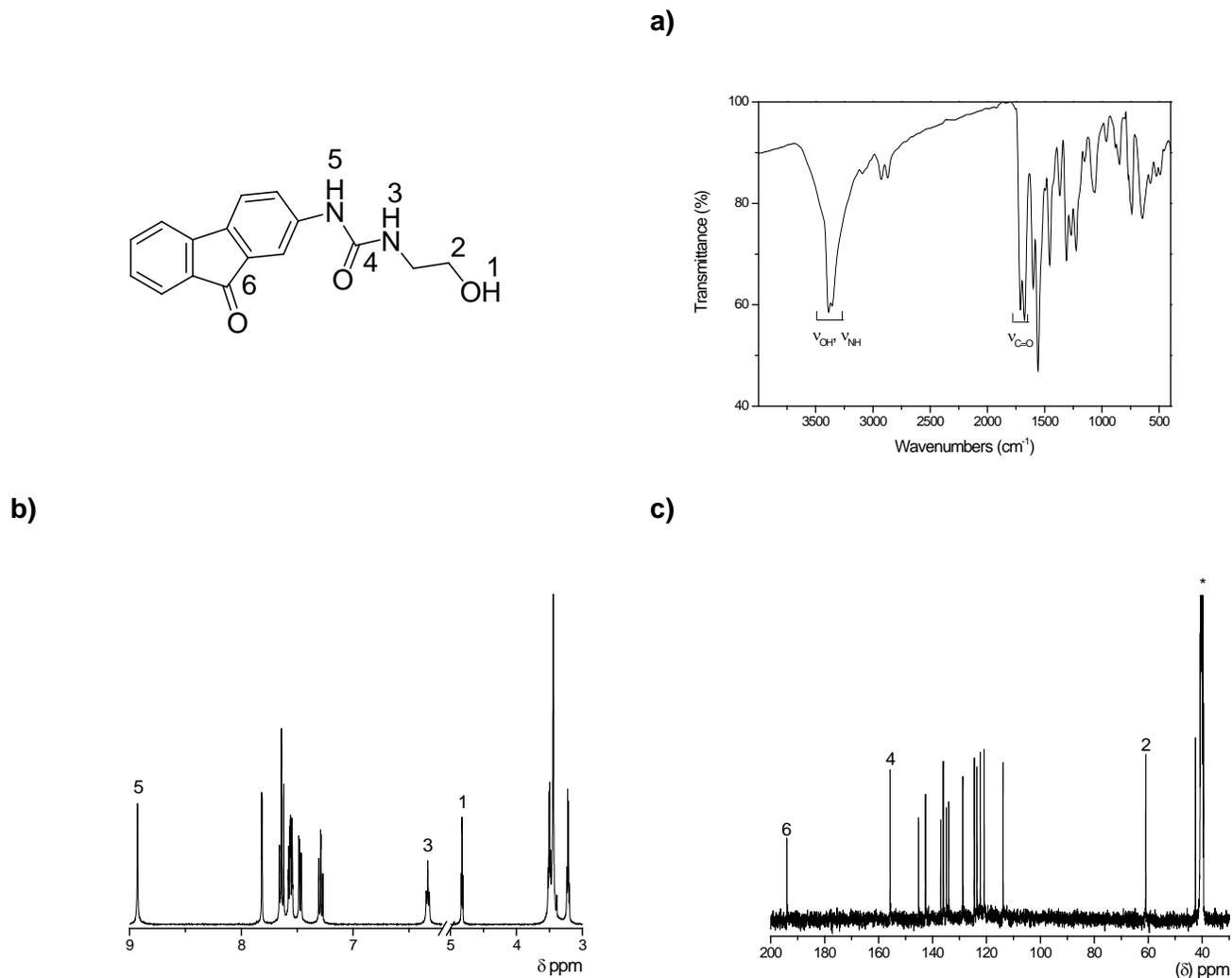


c)



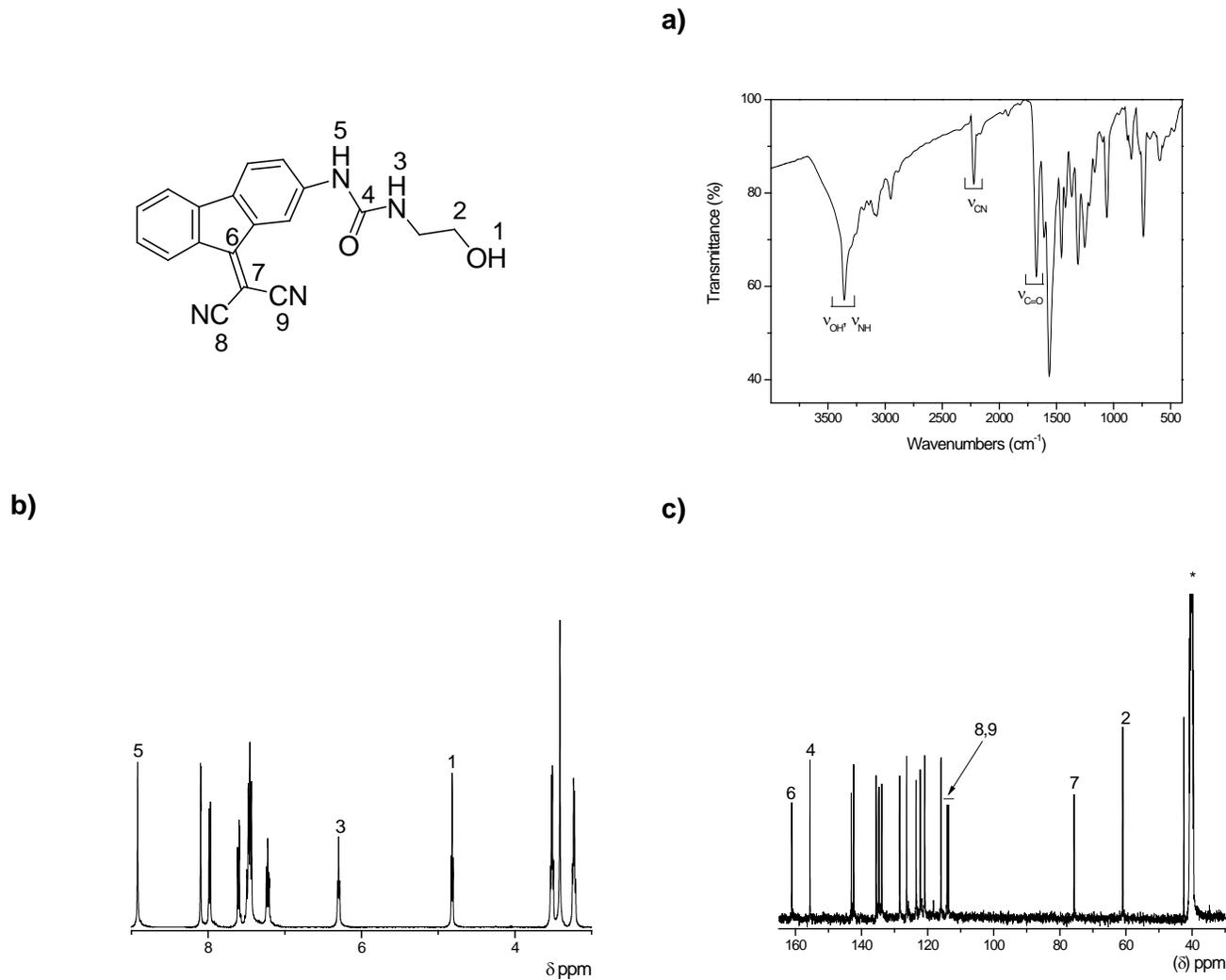
**Figure S1.** Characterization of (**1**) by (a) FTIR, (b) <sup>1</sup>H RMN, and (c) <sup>13</sup>C RMN (\* =solvent signal).

To a 125 mL flask equipped with a reflux condenser was added 13 mmol of 1-(9H-fluoren-7-yl)-3-(2-hydroxyethyl)urea dissolved in 50 mL of DMSO. To the reaction mixture was added 67 mmol of cesium carbonate, and the solution was stirred vigorously at rt for 5 d. Finally, the solution was precipitated in water to give the orange product 1-(2-hydroxyethyl)-3-(9-oxo-9H-fluoren-7-yl)urea. Yield: 98%.



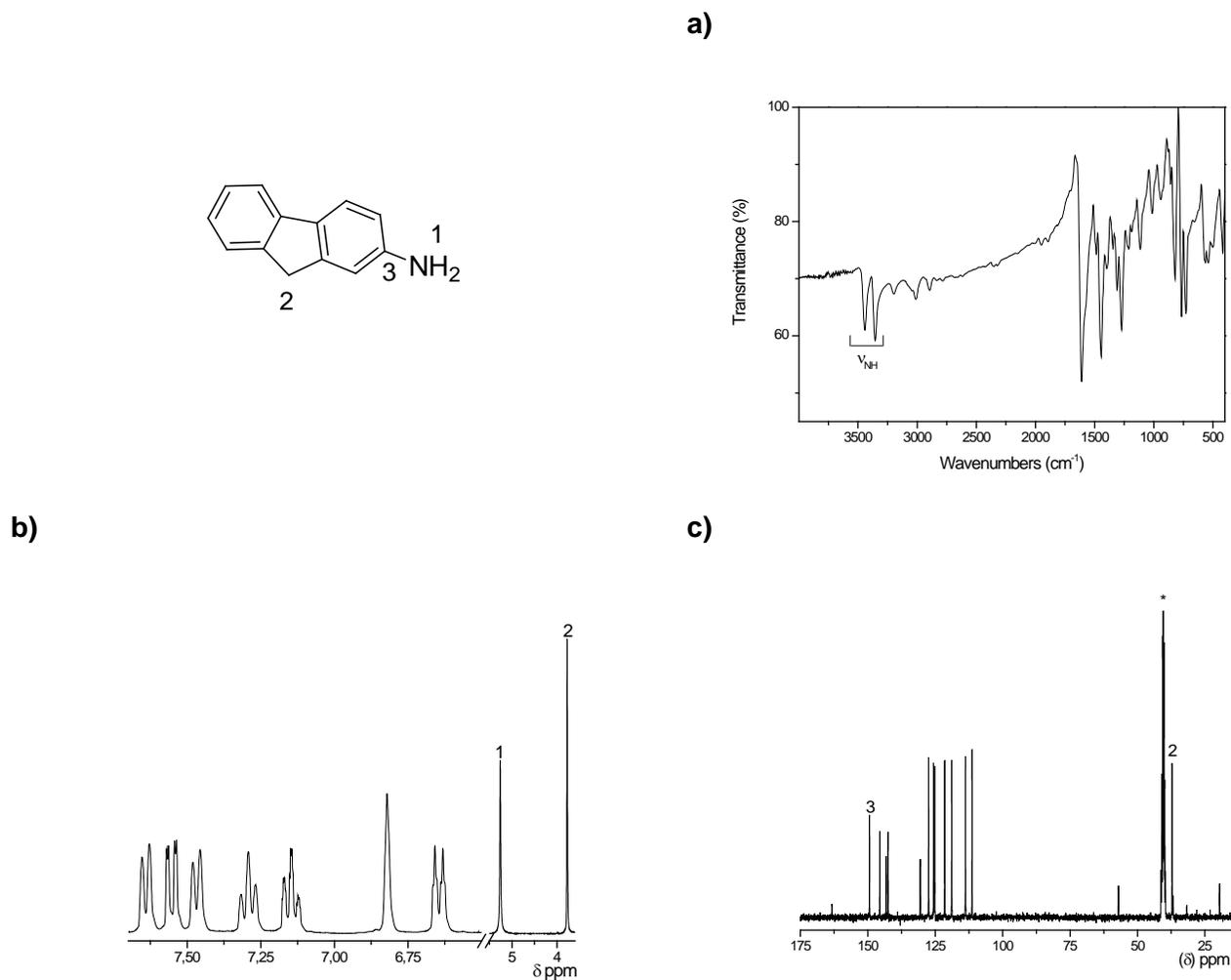
**Figure S2.** Characterization of (**2**) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN (\* =solvent signal).

To a round-bottomed flask fitted with a mechanical stirrer and a reflux condenser was added 16 mmol of 1-(2-hydroxyethyl)-3-(9-oxo-9H-fluoren-7-yl)urea in 50 mL of dimethylformamide (DMF). Subsequently, 30 mmol of malononitrile was added, and the solution was stirred at reflux for 5 d, yielding a precipitate. The precipitate was filtered off and washed with acetone at reflux for 5 min. The product 1-(9-(dicyanomethylene)-9H-fluoren-7-yl)-3-(2 hydroxyethyl)urea was dried thoroughly in a vacuum oven at 60 °C. Yield: 40%.



**Figure S3.** Characterization of (**3**) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN (\* =solvent signal).

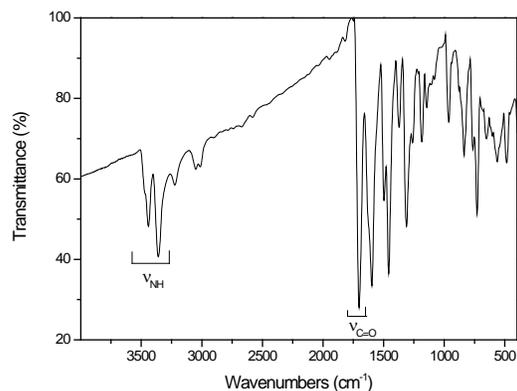
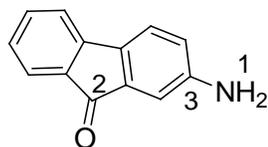
To a hydrogenation flask was added 48 mmol of 2-nitro-9H-fluorene was mixed with in 20 mL of ethanol and 5 g of Pd/C (10% Pd), and the system was purged and pressured with hydrogen to 75 psi. The mixture was stirred at 60 °C for 3 h, and the hydrogen consumed was replaced every 15 min. The solid was filtered off and dried. Yield: 62%.



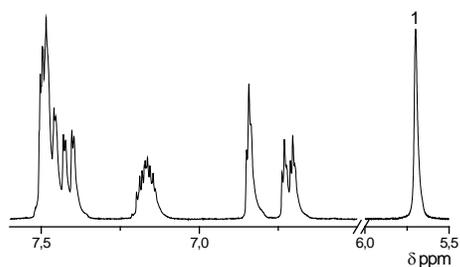
**Figure S4.** Characterization of (4) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN (\* =solvent signal).

To a flask equipped with a reflux condenser was added 30 mmol of 9H-fluoren-2-amine dissolved in 50 mL of DMSO. Subsequently, 89 mmol of cesium carbonate was added, and the solution was vigorously stirred for 5 d at rt. Finally, the solution was precipitated in water, and the garnet product 2-amino-9H-fluoren-9-one was thoroughly washed with water. Yield: 93%.

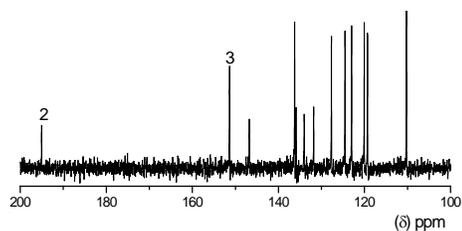
a)



b)

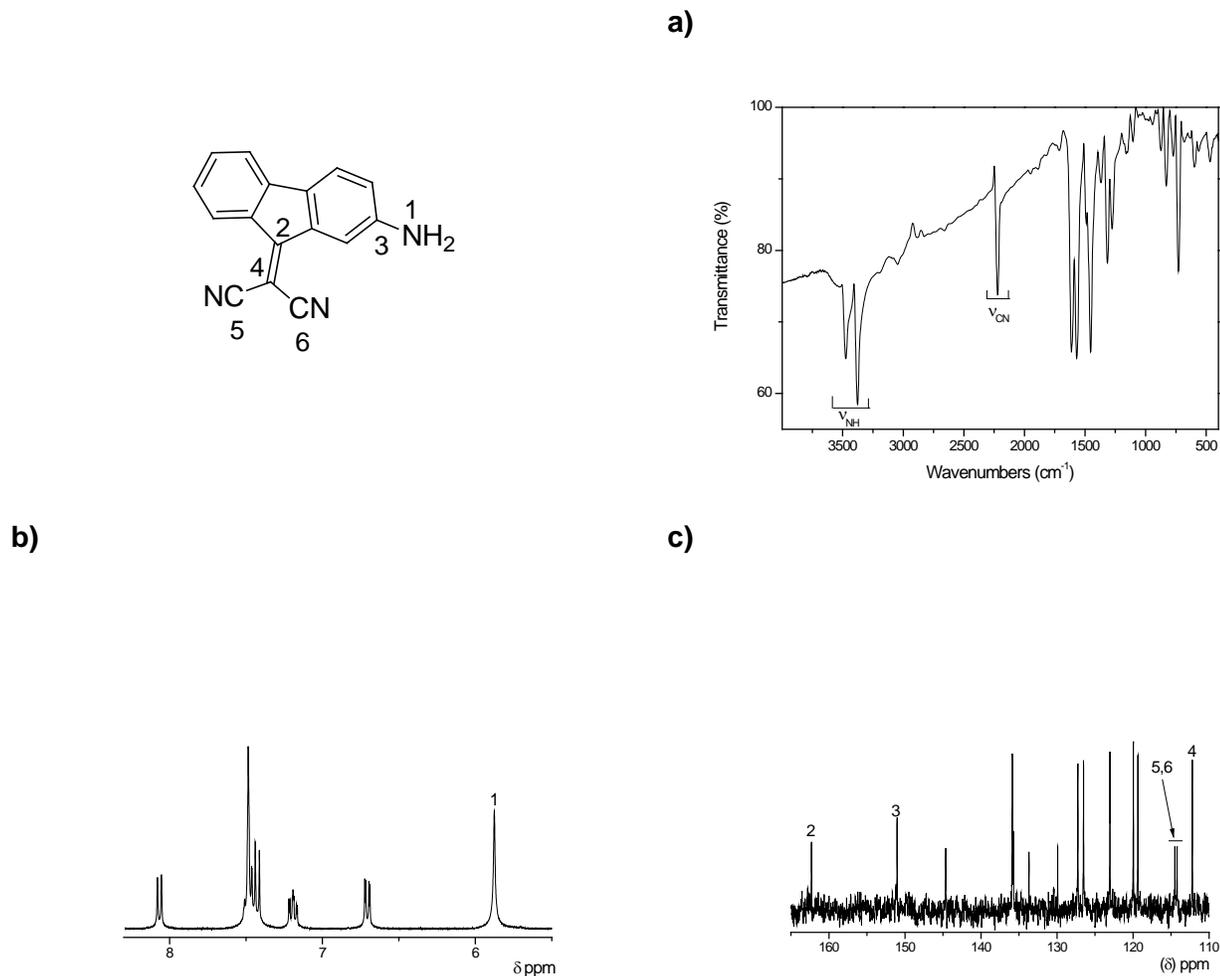


c)



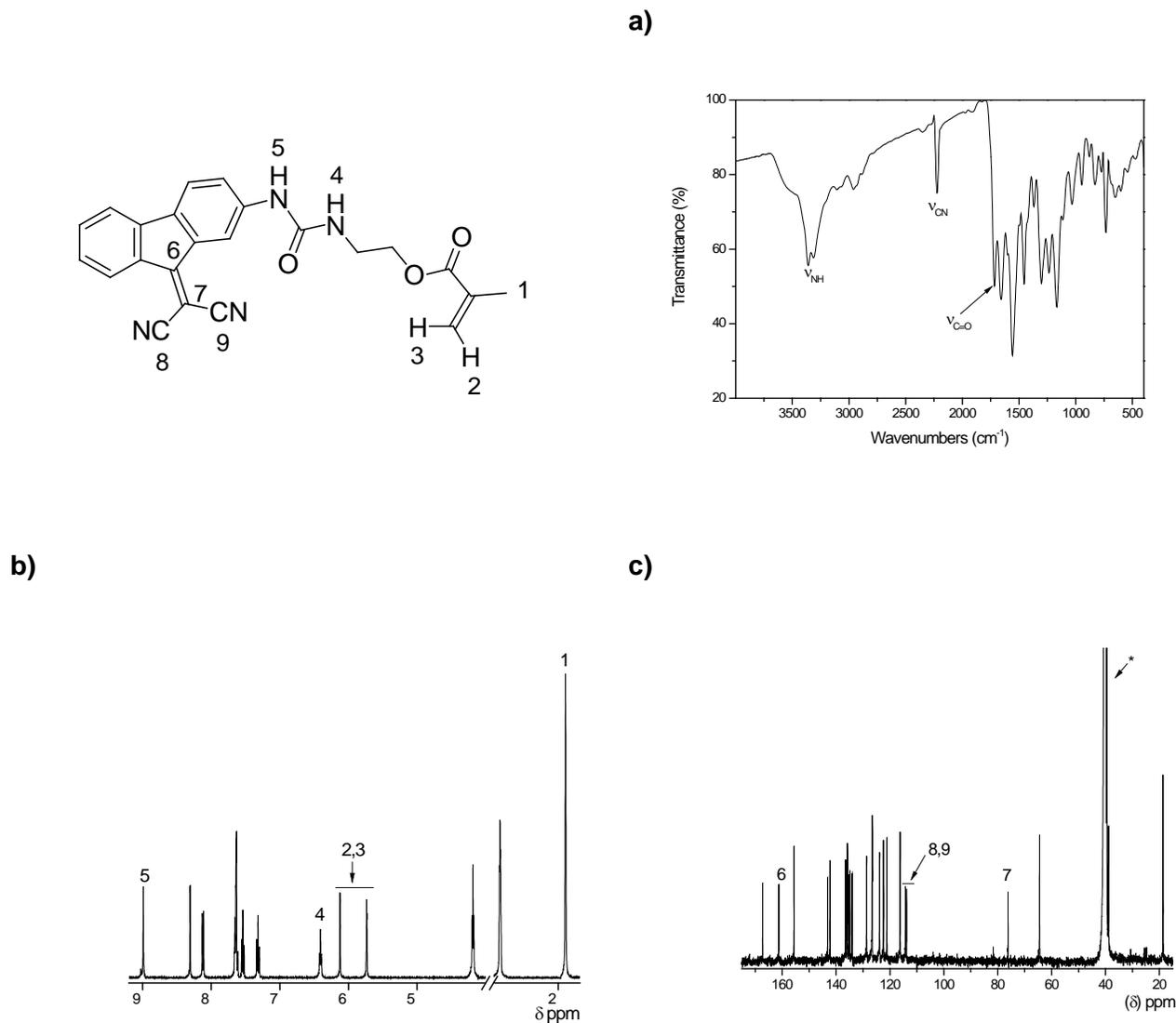
**Figure S5.** Characterization of (5) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN.

To a flask equipped with a reflux condenser was added 8 mmol of 2-amino-9H-fluoren-9-one dissolved in 20 mL of DMF. Afterward, 10 mmol of malononitrile was added portion-wise, and the solution was stirred at reflux for 5 d. The product 2-(2-amino-9H-fluoren-9-ylidene)malononitrile was filtered off and purified by column chromatography with a mixture of hexanes:ethyl acetate (1:1). Yield before purification: 80%. Yield after purification: 25%.



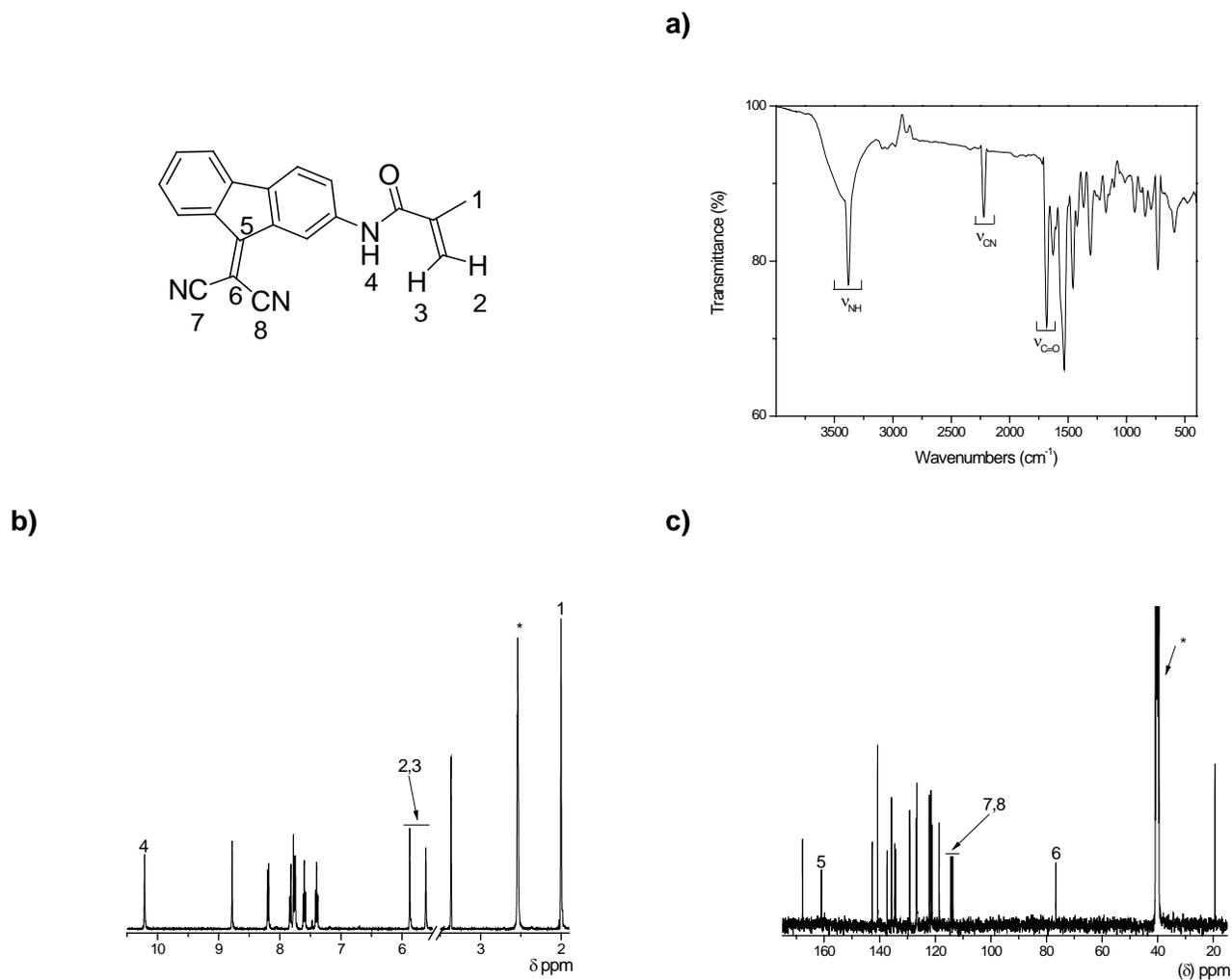
**Figure S6.** Characterization of (**6**) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN.

1.3 mmol of 1-(9-(dicyanomethylene)-9H-fluoren-7-yl)-3-(2-hydroxyethyl)urea was dissolved in 15 mL of pyridine in a round-bottomed flask. Afterward, 1.7 mmol of methacryloyl chloride was added dropwise, and the solution was stirred at room temperature for 3 h. After that, the solution was precipitated in slightly acidified water at 0 °C. The product 2-(3-(9-(dicyanomethylene)-9H-fluoren-7-yl)ureido)ethyl methacrylate was extracted from the crude residue using a Soxhlet apparatus using acetone. The acetone was then removed by distillation, and the product was purified by column chromatography in a mixture of hexane:ethyl acetate (3:1). Yield: 83%.



**Figure S7.** Characterization of (**7**) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN (\* =solvent signal).

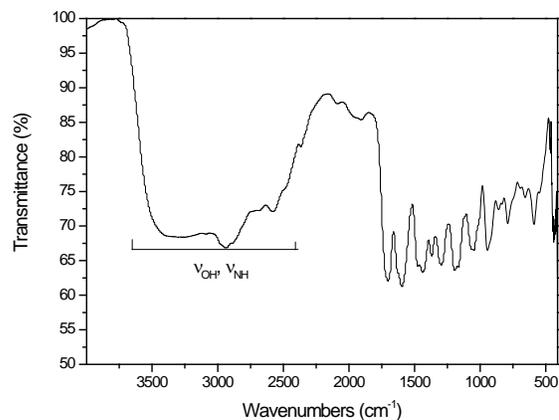
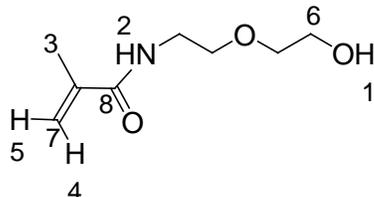
2.1 mmol of 2-(2-amino-9H-fluoren-9-ylidene)malononitrile was dissolved in 8 mL of pyridine in a round-bottomed flask. Afterward, 2.7 mmol of methacryloyl chloride was added dropwise to the solution, and it was stirred at rt for 3 h. The product N-(9-(dicyanomethylene)-9H-fluoren-7-yl)methacrylamide was purified by column chromatography using a mixture of hexane:ethyl acetate (2:1) and was washed in a Soxhlet assembly with ethanol. Yield before purification: 87%. Yield after purification: 20%.



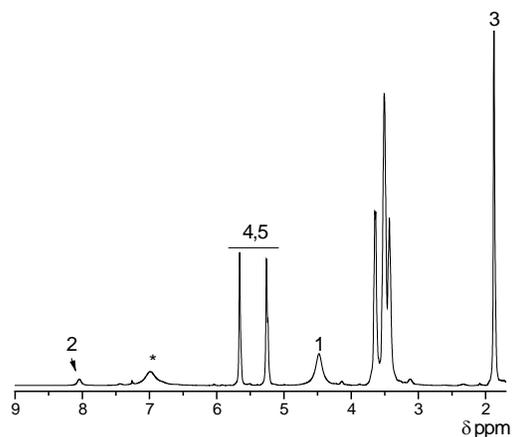
**Figure S8.** Characterization of (**8**) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN (\* =solvent signal).

To 20 mL of an ice-cold, methanolic solution of 2-(2-aminoethoxyethanol) (2.4 mL, 24 mmol) was slowly added 2.4 mL (25 mmol) of methacryloyl chloride diluted in 20 mL of THF under a nitrogen blanket. Potassium hydroxide (1 M, aqueous) was added to maintain a pH of 8-9 throughout the reaction. The mixture was warmed to rt over 4 h. Afterwards, it was quenched by addition of hydrochloric acid to a final pH of 5, and the product was concentrated. Finally, to the crude residue was added sodium chloride, and it was extracted with dichloromethane. Yield: 97%.

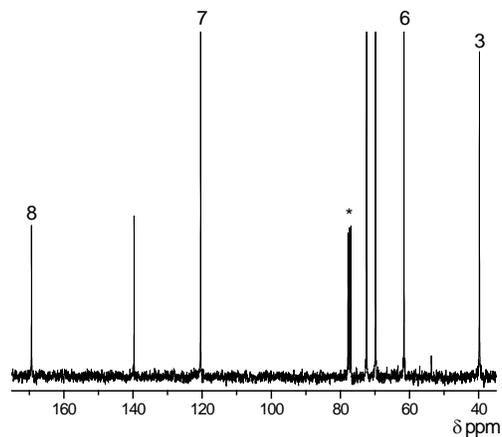
a)



b)

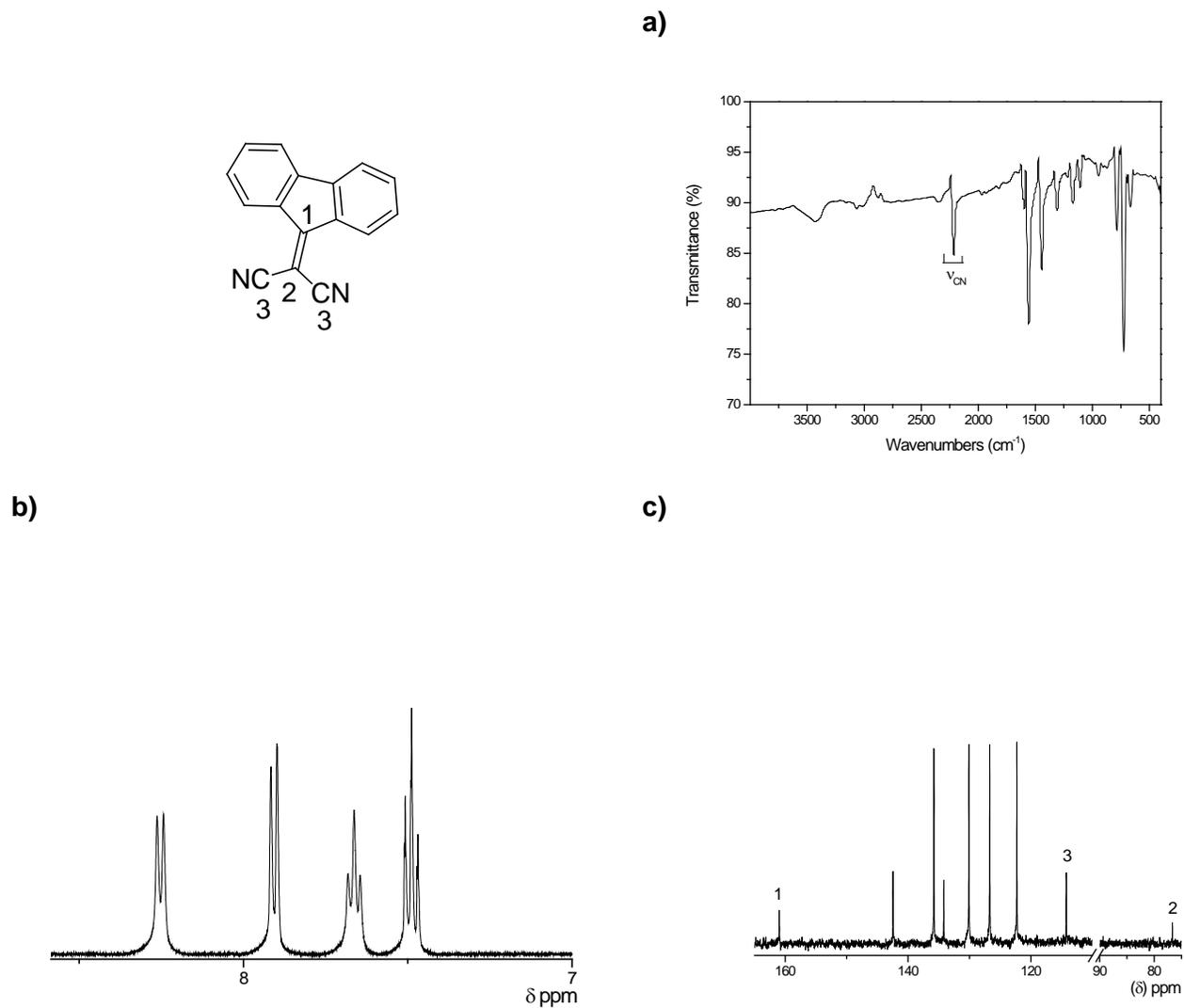


c)



**Figure S9.** Characterization of (**9**) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN. (\* =solvent signal).

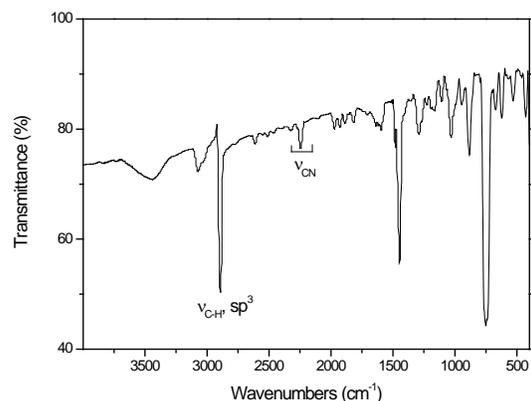
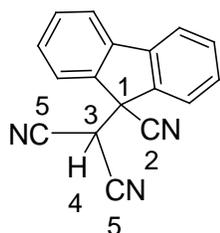
11 mmol of 9H-fluoren-9-one was dissolved in 25 mL of DMF. Afterward, 16.5 mmol of malononitrile was added, and the solution was stirred at reflux for 5 d. The solution was precipitated in water, and the solid was recrystallized from acetone.



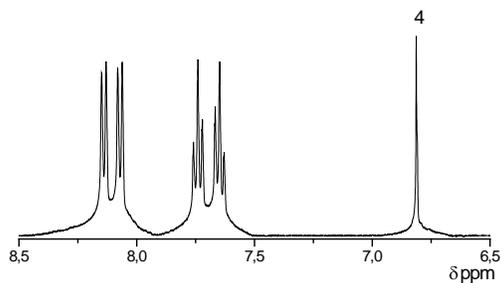
**Figure S10.0** Characterization of (**10**) by (a) FTIR, (b)  $^1\text{H}$  RMN, and (c)  $^{13}\text{C}$  RMN.

8.8 mmol of 2-(9H-fluoren-9-ylidene)malononitrile was dissolved in 15 mL of DMSO. Afterward, 17.6 mmol of sodium cyanide was added, and the solution was stirred at rt for 2 h. The solution was precipitated in water, and the solid was filtered off and washed with water. The product 9-(dicyanomethyl)-9H-fluorene-9-carbonitrile was dried in a vacuum oven at 60 °C.

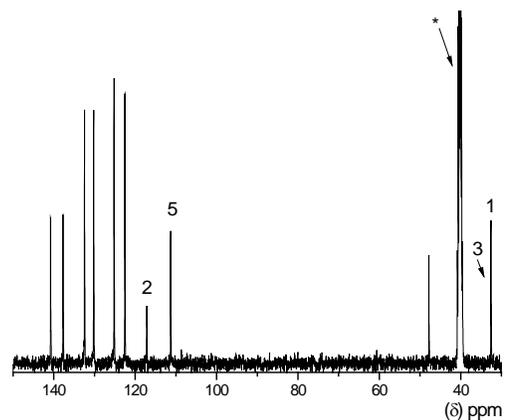
a)



b)



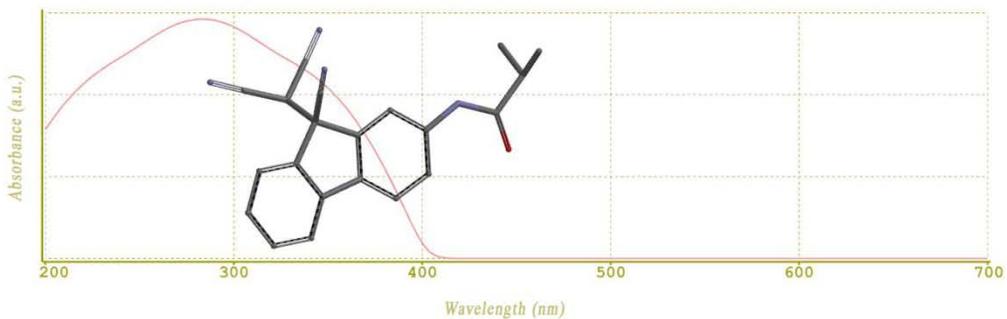
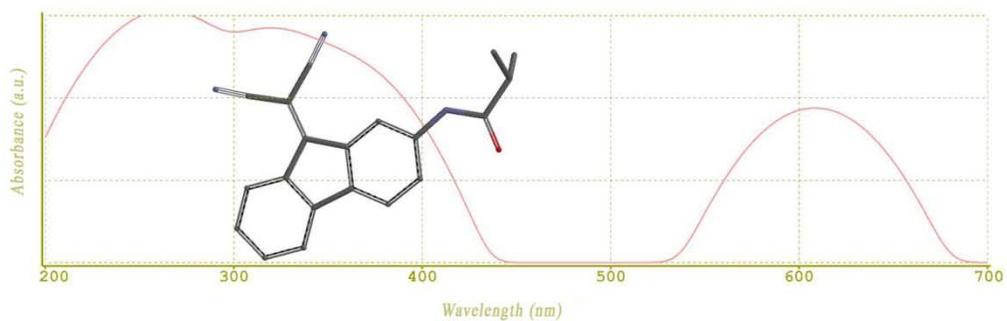
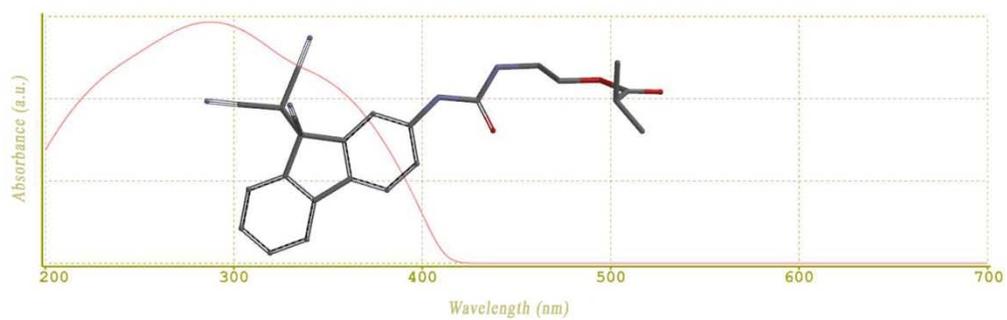
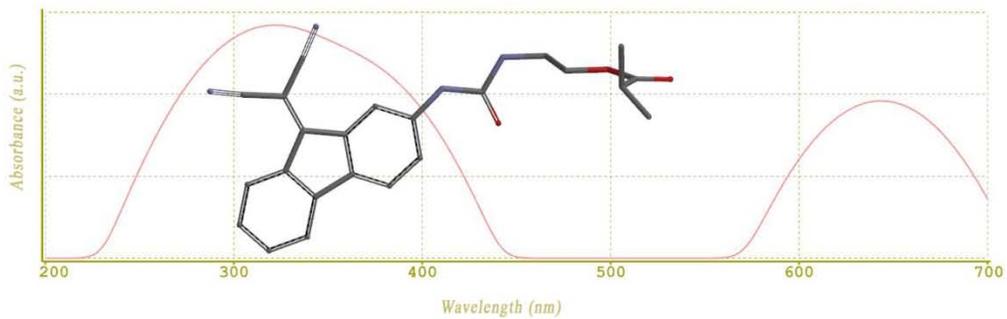
c)



**Figure S11.** Characterization of (**11**) by (a) FTIR, (b) <sup>1</sup>H RMN, and (c) <sup>13</sup>C RMN ( \* =solvent signal).

S3. Theoretical calculation of UV-Vis spectra of model molecules (UV-Vis DFT calculations at B3LYP/6-31G)

Published in *Journal of Physical Chemistry*  
The Royal Society of Chemistry 2010



The membranes were prepared by radical polymerization of mixtures of the 4 different co-monomers using ethylene glycol dimethacrylate as cross-linking agent (1%) and AIBN (1 wt %) as a thermal radical initiator. Eight different polymer films were prepared in this fashion by varying the molar concentration of monomers. The reactions were carried out in silanized glass molds of 100 mm thickness in an oxygen-free atmosphere at 65 °C for 5 h.

#### S5. Measurements and instrumentation

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively, using DMSO- $d_6$  as the solvent.

Infrared spectra (FT-IR) were recorded using a Nicolet Impact spectrometer.

The UV–Vis spectra were recorded using a Varian Cary3-Bio UV–Vis spectrophotometer.

The apparent response time was recorded using a digital stopwatch. The different polymeric films were dipped in a water solution of sodium cyanide (3 M), and the time was taken when the color of the film turned colorless to the naked eye. Each experiment was repeated three times, and the results were averaged.