

Electronic Supplementary Information

For the manuscript

Photocatalytic Hydrogen Evolution Through Fully Conjugated Poly(azomethine) Networks

by

**Matthias Georg Schwab,^a Manuel Hamburger,^a Jie Shu,^a
Hans Wolfgang Spiess,^a Xinchen Wang,^{*b} Markus Antonietti,^b
Xinliang Feng^a and Klaus Müllen^{*a}**

^aMax Planck Institute for Polymer Research
Ackermannweg 10, D-55128 Mainz, Germany
muellen@mpip-mainz.mpg.de

^bMax Planck Institute of Colloids and Interfaces
Research Campus Golm, D-14424 Potsdam, Germany
xinchen.wang@mpikg.mpg.de

Materials and methods

Unless otherwise noted, all starting materials were purchased from Aldrich, Acros and TCI. The compounds were used as received without further purification.

Naphthalene-2,6-dicarbaldehyde¹ and anthracene-9,10-dicarbaldehyde² were prepared according to literature-known procedures in 71 % and 58 % yield, respectively.

Photocatalytic reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. H₂ production was performed by dispersing 100 mg of **ANW** catalyst powder in 100 ml of an aqueous solution containing triethanolamine (10 vol%). For the deposition of platinum, an appropriate amount of H₂PtCl₆ was dissolved in the catalyst solution. The solution was evacuated several times to remove air completely prior to irradiation under a 300 W xenon lamp and a water filter. The wavelength of the incident light ($\lambda > 300$ nm) was controlled by using an appropriate cut-off filter. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography. The experimental error in the rate of H₂ evolution was within 15 %.

Fourier transform infrared (FTIR) spectra were collected with a Nicolet 730 spectro-meter, equipped with an attenuated total reflection (ATR) setup.

Solid-state ¹³C [¹H] cross-polarization (CP) NMR spectra were recorded on a Bruker ASX 500 instrument equipped with a 2.5mm MAS double ¹H-X probe at a Larmor frequency of 125.8 MHz for ¹³C. The samples were packed in 2.5mm rotors and experienced fast magic angle spinning (MAS) at the rate of 25 kHz. The ¹⁵N [¹H] CP spectra were obtained on a Bruker DSX 300 instrument at 21.7 MHz for ¹⁵N. The samples were packed in 4mm rotors and the MAS rate was 10 kHz. The ¹³C and ¹⁵N CP measurements were performed using a contact time of 3 ms and 7 ms, respectively. Two-pulse, phase modulation (TPPM) sequence was introduced as a ¹H decoupling method at the power of 100 kHz. Both of the ¹³C and ¹⁵N NMR spectra were referenced with respect to tetramethyl silane using adamantane (¹³C, 29.456 ppm) and nitromethane (¹⁵N, -358.4 ppm) as secondary standards. All the spectra were acquired at room temperature with accumulations of 6000 and 30000 scans for ¹³C and ¹⁵N spectra.

DFT calculations were performed with ORCA, B3LYP being the (hybrid) exchange functional, employing 6-311G** as basis set. A representative linear fragment of the **ANW** network

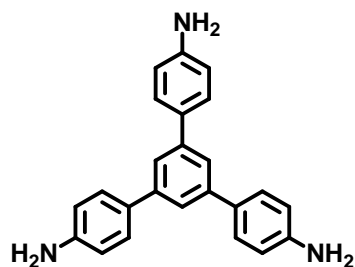
structure was chosen and its geometry optimized (gas phase). It should be noted however that these fragments may be heavily distorted in the network formed during polymerization.

Experimental section

General considerations

The **ANW** networks were synthesized at fixed molar ratio of amine to aldehyde groups of 1.15 / 1.00 to allow for efficient cross-linking.

Synthesis of 1,3,5-tris(4-aminophenyl)benzene



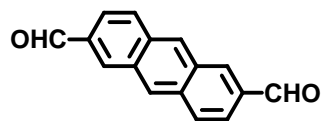
2.0 g (6.35 mmol) of 1,3,5-tribromobenzene and (4-aminophenyl)boronic acid were dissolved in 50 ml of toluene. Then, a few drops of Aliquat 336 and 15.0 ml of an aqueous K_2CO_3 (2 M) were added. After degassing by argon bubbling, 0.11 g (0.095 mmol) of tetrakis(triphenylphosphine)palladium(0) were added. The reaction mixture was heated to 100 °C for 24 h. The crude product was purified by column chromatography (hexane/ethyl acetate 7/3) to yield 1.38 g (3.937 mmol) of 1,3,5-tris(4-aminophenyl)benzene in 62 % as an off-white solid.

1H NMR (300 MHz, CD_2Cl_2) δ 7.59 (s, 3H), 7.51 (dd, J = 2.1, 8.7, 6H), 6.77 (dd, J = 2.2, 8.7, 6H), 3.82 (s, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 146.79, 142.32, 131.69, 128.39, 122.80, 115.49.

MS (FD, 8kV): m/z (%) = 350.8 (100.0 %, M^+), (calc. for $C_{24}H_{21}N_3$ = 351.17 g mol $^{-1}$).

Synthesis of anthracene-2,6-dicarbaldehyde



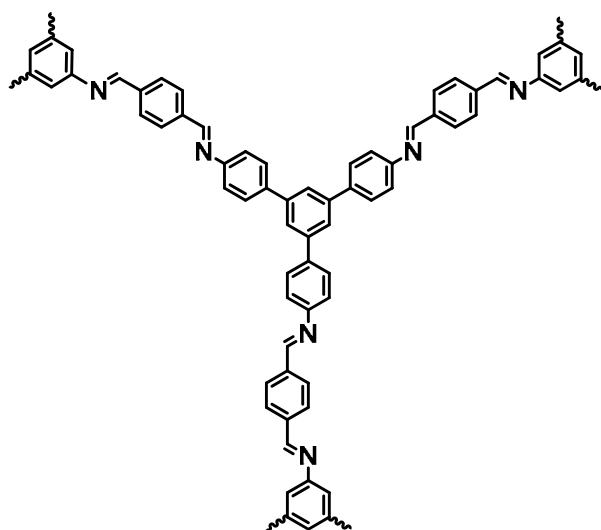
0.50 g (1.48 mmol) of 2,6-dibromoanthracene was placed in a flame-dried Schlenk tube which was subsequently evacuated and refilled with argon for three times. 15.0 ml of dry tetrahydrofuran were added and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. Then, 21.4 mmol ml of *n*-butyllithium (1.6 M in hexane) was added and the reaction was allowed to proceed for 1 h at this temperature. 10.0 ml of anhydrous dimethyl formamide were added and the mixture was stirred for 1 h. The mixture was slowly brought to room temperature and quenched by the addition of methanol/water. The crude product was purified by column chromatography (hexane, hexane/ethyl acetate 7/3) and recrystallized from toluene/ethanol to yield 0.22 g (0.94 mmol) of anthracene-2,6-dicarbaldehyde in 61 % as a yellow crystalline solid.

$^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 10.21 (s, 2H), 8.72 (s, 2H), 8.58 (s, 2H), 8.18 (d, $J = 9.1$, 2H), 7.97 (d, $J = 8.8$, 2H).

$^{13}\text{C NMR}$ (176 MHz, CD_2Cl_2) δ 192.16, 136.78, 135.43, 134.23, 132.76, 130.15, 129.70, 122.15.

MS (FD, 8kV): m/z (%) = 233.2 (100.0 %, M^+), (calc. for $\text{C}_{16}\text{H}_{10}\text{O}_2 = 351.17\text{ g mol}^{-1}$).

Synthesis of ANW 1

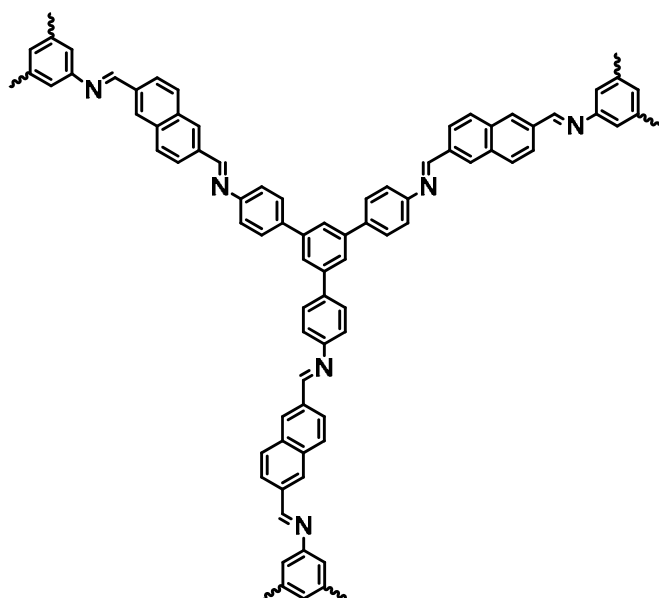


250 mg (0.71 mmol) of 1,3,5-tris(4-aminophenyl)benzene and 125 mg (0.93 mmol) of terephthalaldehyde were placed in a Schlenk tube. Then, 10.0 ml of dioxane and 2.2 ml of acetic acid (3 M) were added and the mixture was degassed by argon bubbling. The reaction

mixture was heated to reflux for 3 d. The yellow precipitate was collected by filtration and subjected to Soxhlet extraction in tetrahydrofuran for 24 h to yield 276 mg (82 %) of **ANW 1**.

Elemental analysis: for $C_{72}H_{42}N_6$, calculated: C, 87.25; H, 4.27; N, 8.48 %. Found: C, 82.06 ; H, 3.55; N, 7.70 %.

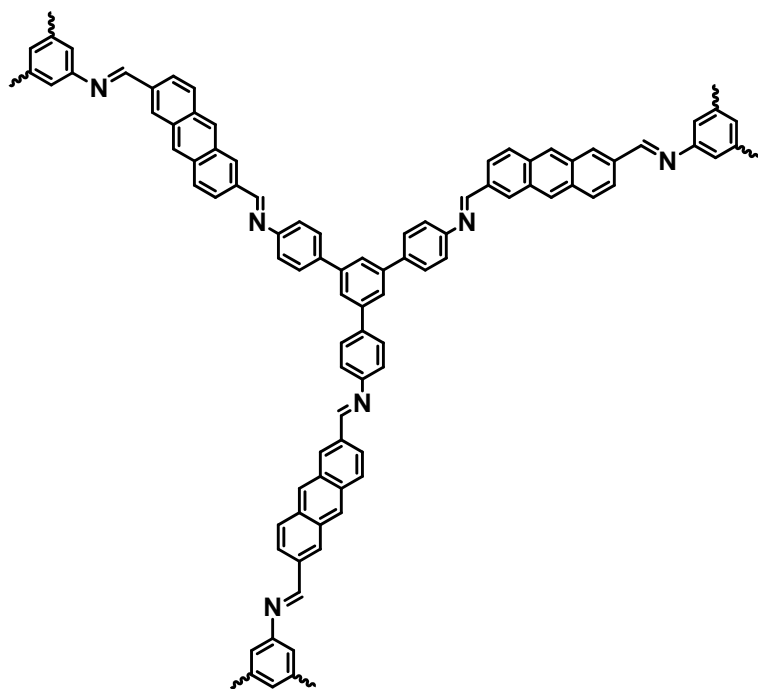
Synthesis of ANW 2



250 mg (0.71 mmol) of 1,3,5-tris(4-aminophenyl)benzene and 171 mg (0.93 mmol) of naphthalene-2,6-dicarbaldehyde were placed in a Schlenk tube. Then, 10.0 ml of dioxane and 2.2 ml of acetic acid (3 M) were added and the mixture was degassed by argon bubbling. The reaction mixture was heated to reflux for 3 d. The orange-yellow precipitate was collected by filtration and subjected to Soxhlet extraction in tetrahydrofuran for 24 h to yield 291 mg (76 %) of **ANW 2**.

Elemental analysis: for $C_{84}H_{48}N_6$, calculated: C, 88.40; H, 4.24; N, 7.36 %. Found: C, 84.63 ; H, 4.28; N, 6.98 %.

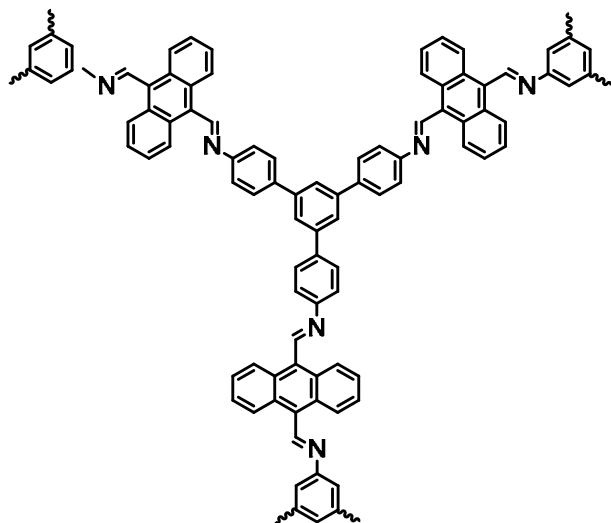
Synthesis of ANW 3



150 mg (0.43 mmol) of 1,3,5-tris(4-aminophenyl)benzene and 131 mg (0.56 mmol) of anthracene-2,6-dicarbaldehyde were placed in a Schlenk tube. Then, 10.0 ml of dioxane and 2.1 ml of acetic acid (3 M) were added and the mixture was degassed by argon bubbling. The reaction mixture was heated to reflux for 3 d. The orange-yellow precipitate was collected by filtration and subjected to Soxhlet extraction in tetrahydrofuran for 24 h to yield 180 mg (70 %) of **ANW 3**.

Elemental analysis: for $C_{96}H_{54}N_6$, calculated: C, 89.28; H, 4.21; N, 6.51 %. Found: C, 81.55; H, 5.23; N, 6.21 %.

Synthesis of ANW 4



150 mg (0.43 mmol) of 1,3,5-tris(4-aminophenyl)benzene and 131 mg (0.56 mmol) of anthracene-9,10-dicarbaldehyde were placed in a Schlenk tube. Then, 6.0 ml of dioxane and 1.3 ml of acetic acid (3 M) were added and the mixture was degassed by argon bubbling. The reaction mixture was heated to reflux for 3 d. The red-orange precipitate was collected by filtration and subjected to Soxhlet extraction in tetrahydrofuran for 24 h to yield 185 mg (72 %) of **ANW 4**.

Elemental analysis: for $C_{96}H_{54}N_6$, calculated: C, 89.28; H, 4.21; N, 6.51 %. Found: C, 85.10; H, 3.66; N, 5.52 %.

Fourier transform infrared (FTIR) spectroscopy

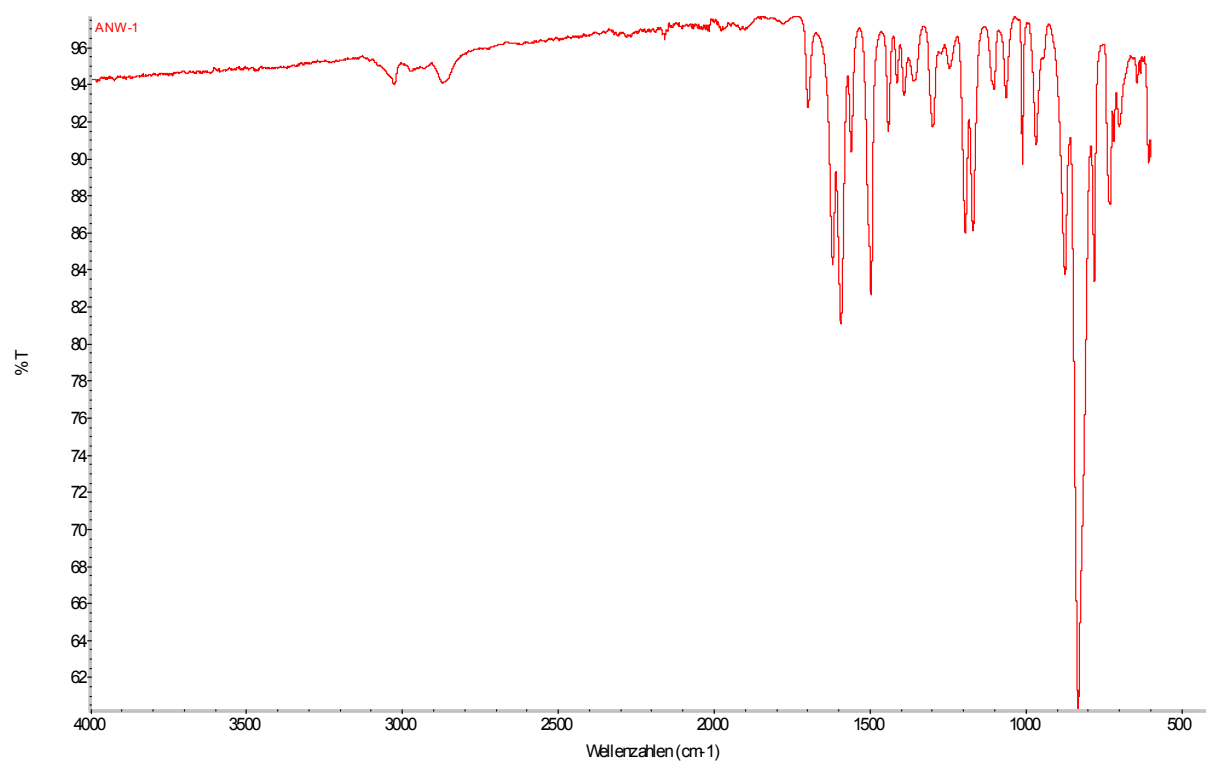


Figure S1. Fourier transform infrared (FTIR) spectra of ANW 1.

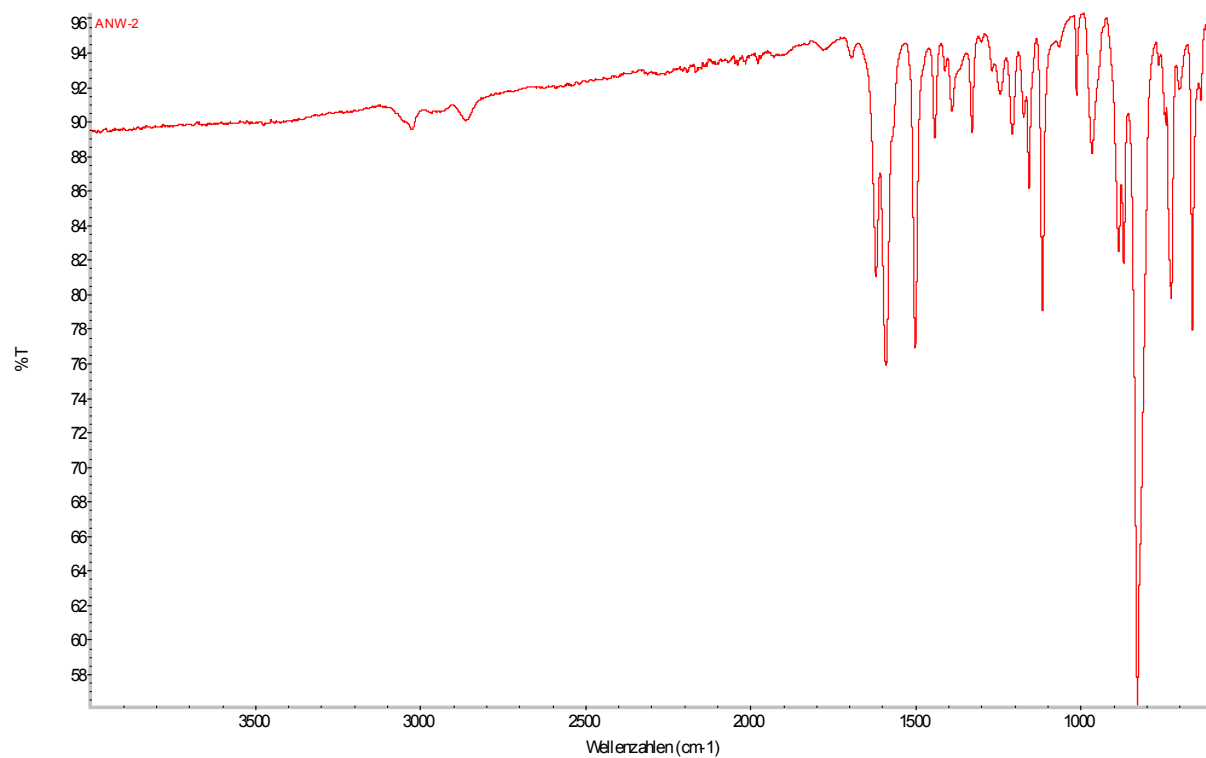


Figure S2. Fourier transform infrared (FTIR) spectra of ANW 2.

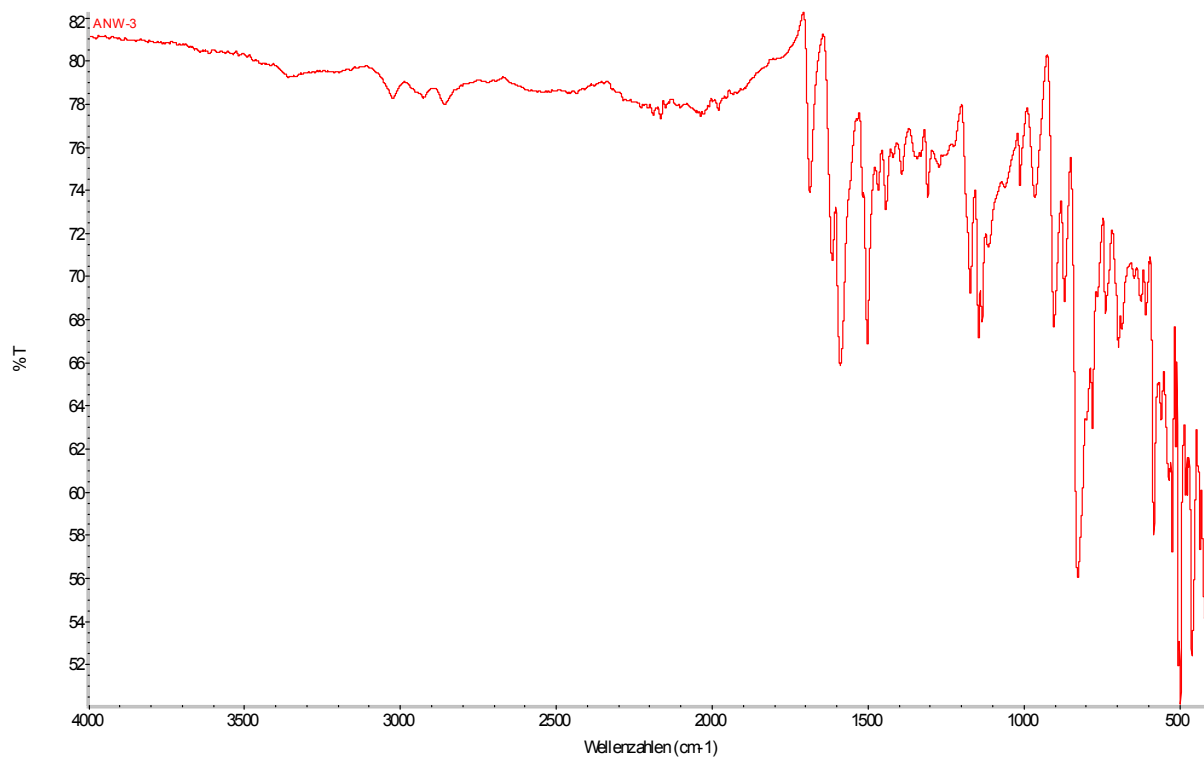


Figure S3. Fourier transform infrared (FTIR) spectra of ANW 3.

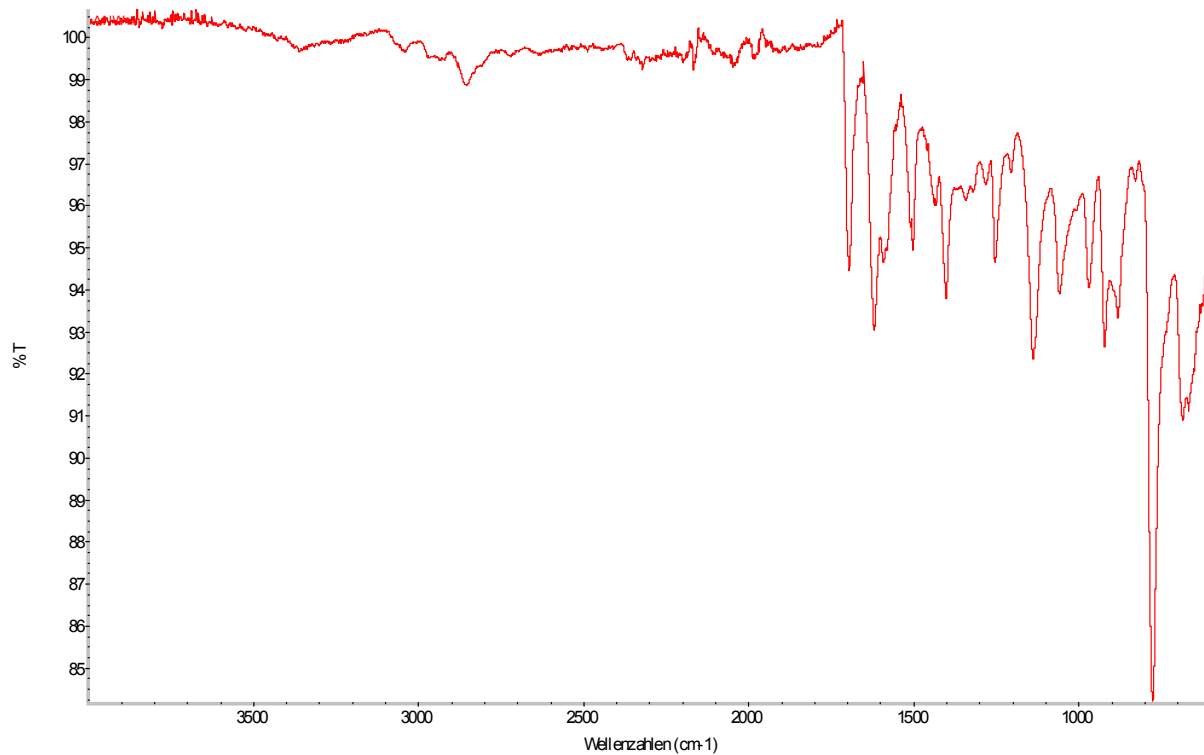


Figure S4. Fourier transform infrared (FTIR) spectra of ANW 4.

Solid-state NMR spectroscopy

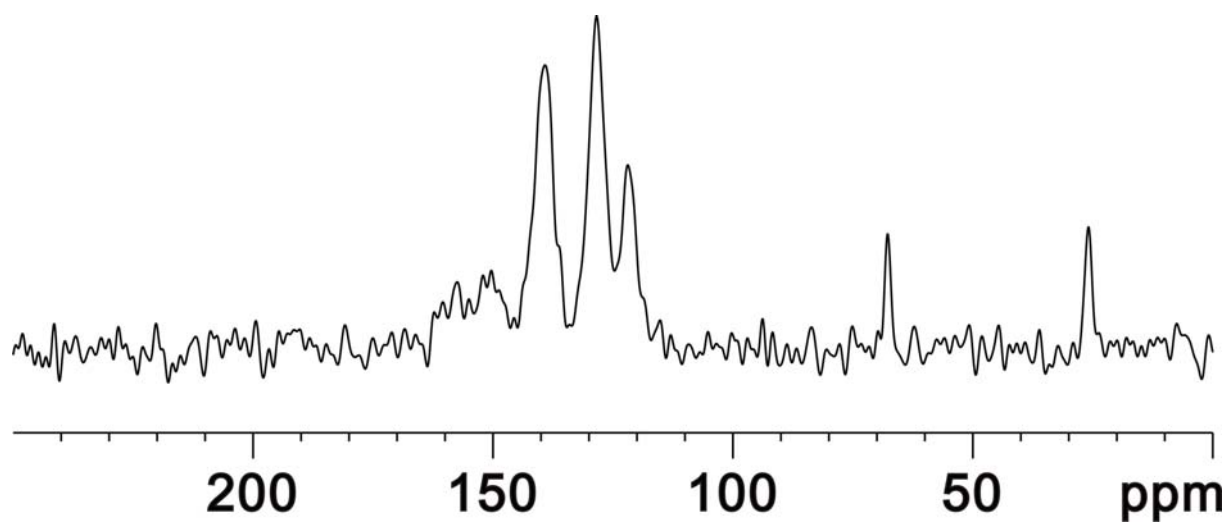


Figure S5. Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of ANW 1.

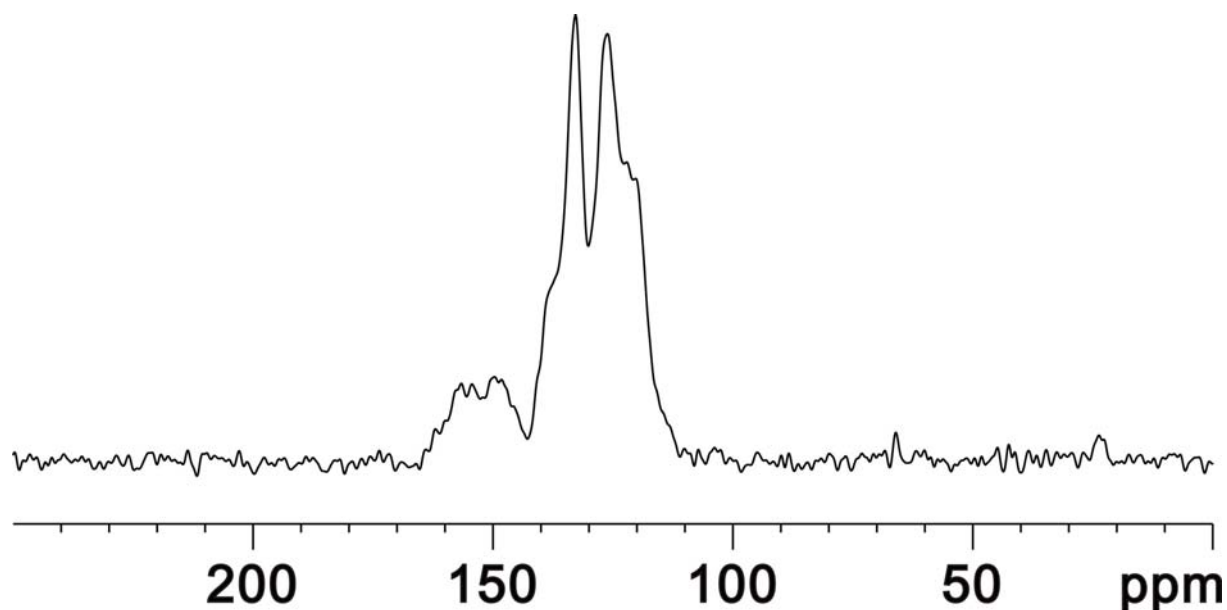


Figure S6. Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of ANW 2 (*before catalysis*).

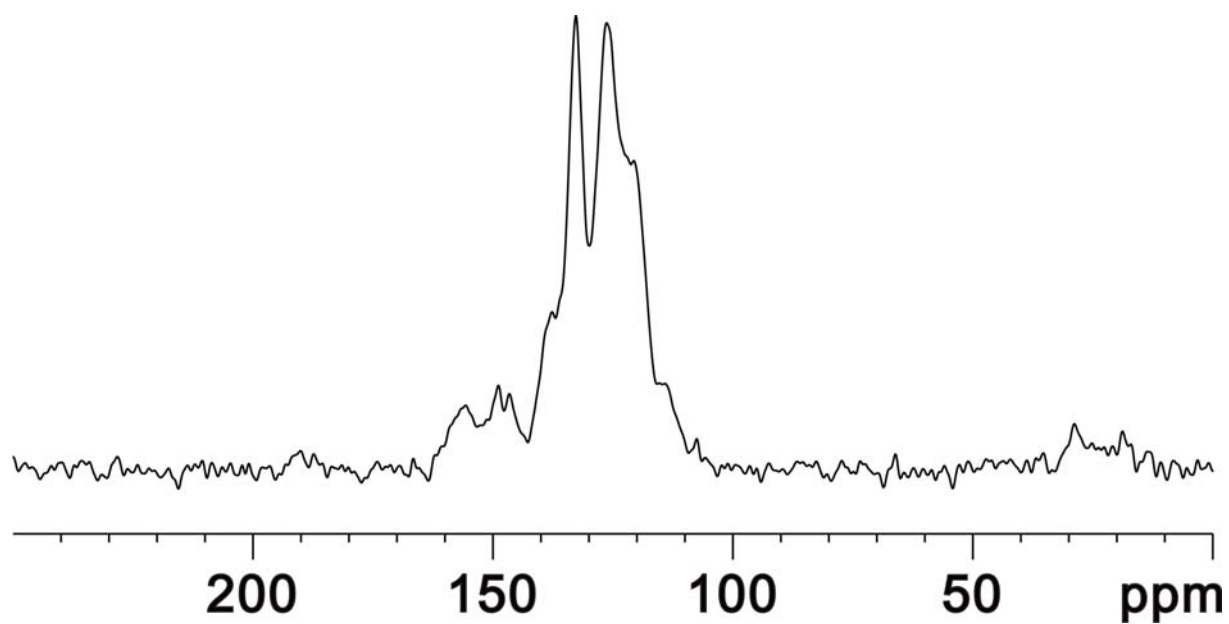


Figure S7. Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of ANW 2 (after catalysis).

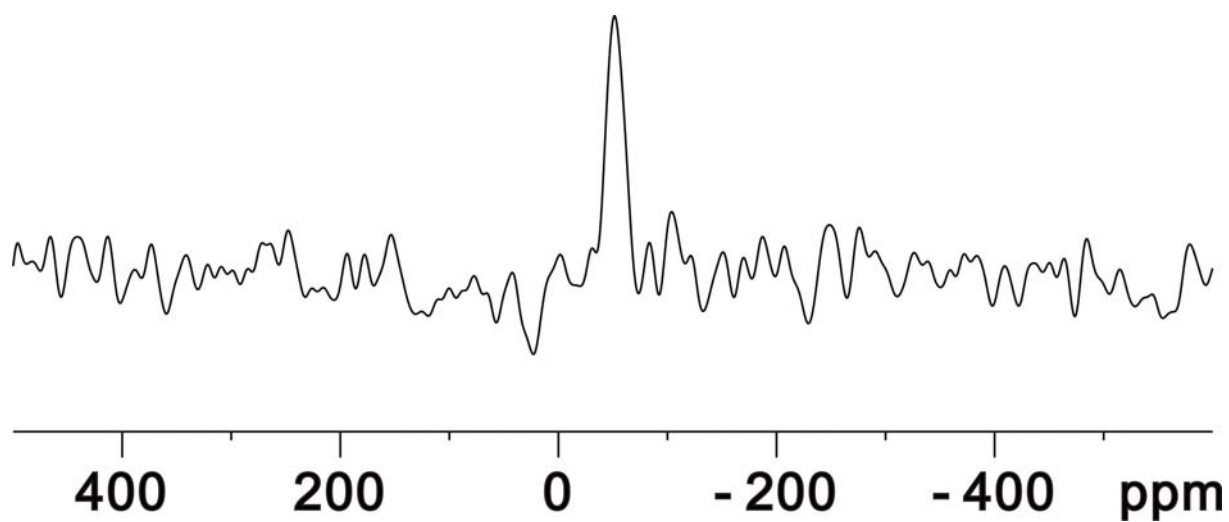


Figure S8. Cross-polarization (CP) ^{15}N MAS natural abundance NMR spectrum of ANW 2.

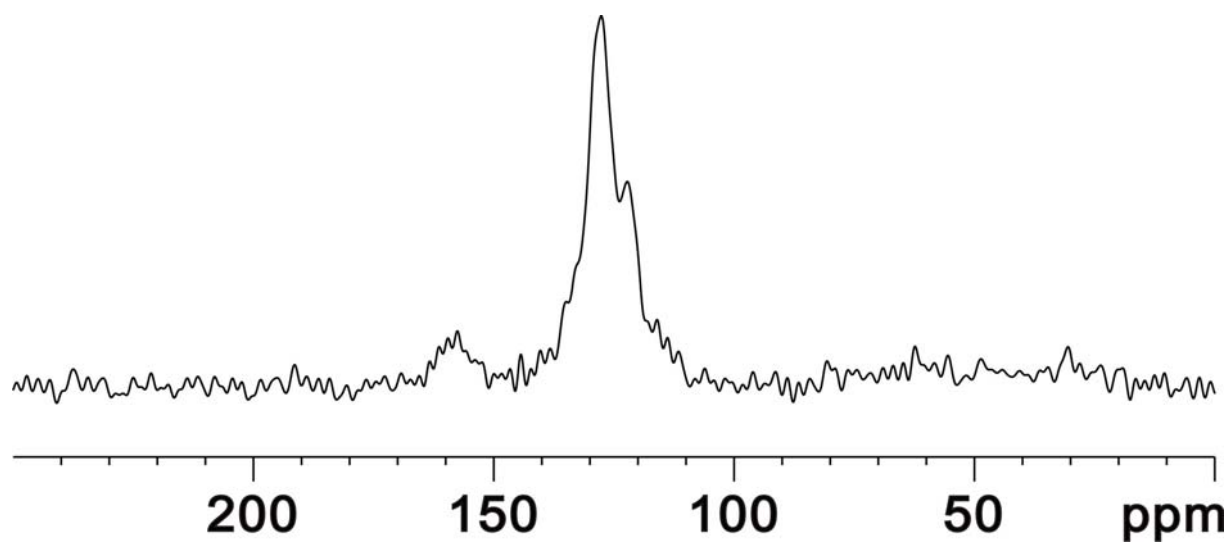


Figure S9. Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of ANW 3.

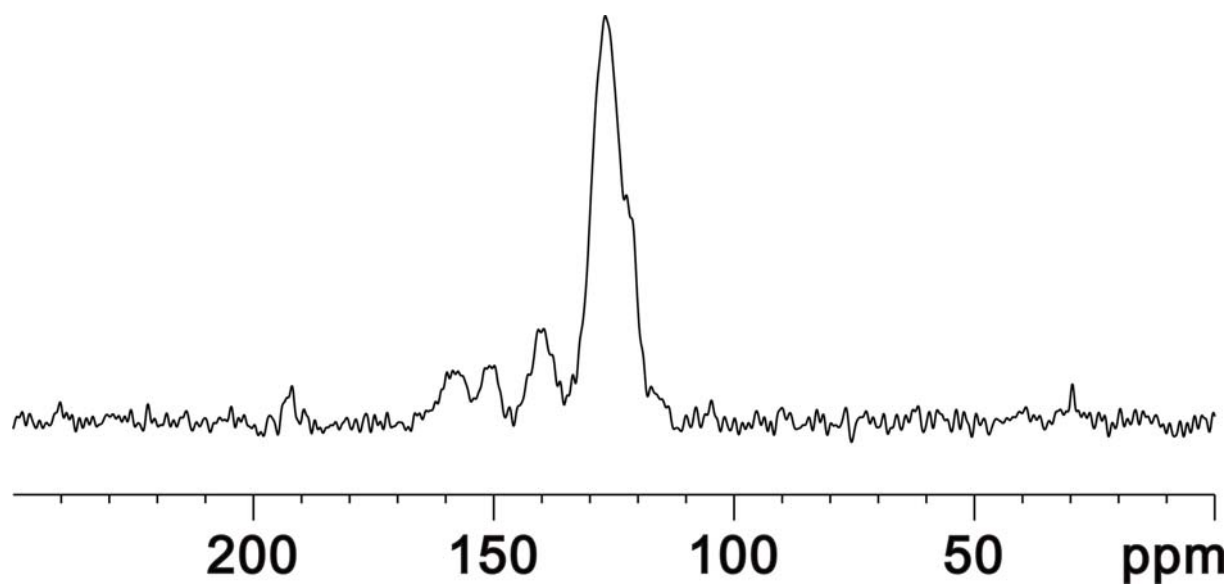


Figure S10. Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of ANW 4.

DFT Calculations

	HOMO [eV]	LUMO [eV]	HOMO-LUMO gap [eV]	Dipole moment [D]	Torsional angles [°]
ANW-1	-5.84	-2.48	3.36	0.11	0.5/0.6
ANW-2	-5.77	-2.51	3.26	0.16	1.2/2.1
ANW-3	-5.55	-2.68	2.87	0.14	0.9/1.7
ANW-4	-5.53	-2.80	2.73	0.16	29.5/34.9

Table S1. DFT calculation summary for ANW 1-4.

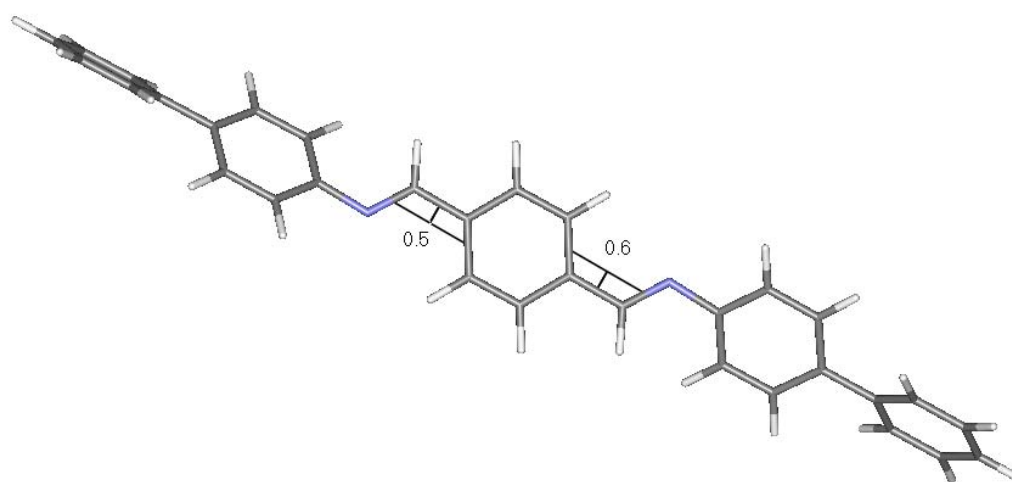


Figure S11. DFT calculation and torsion angles of the model segment of ANW 1.

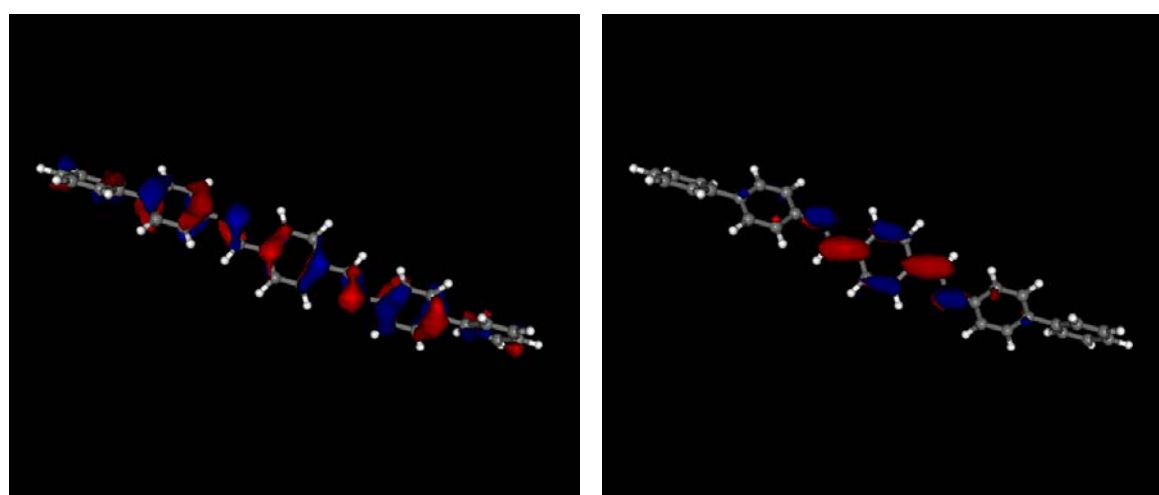


Figure S12. DFT calculation and torsion angles of the model segment of ANW 1.

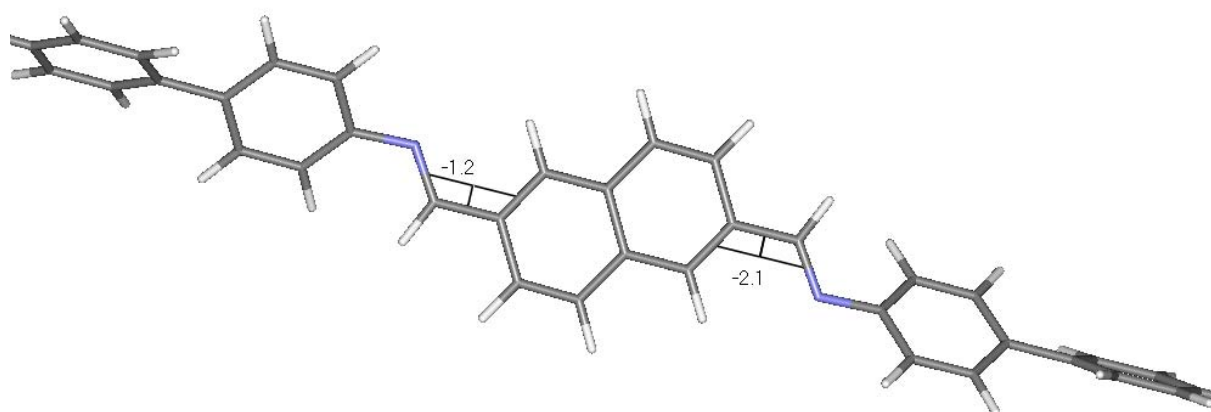


Figure S13. DFT calculation and torsion angles of the model segment of ANW 2.

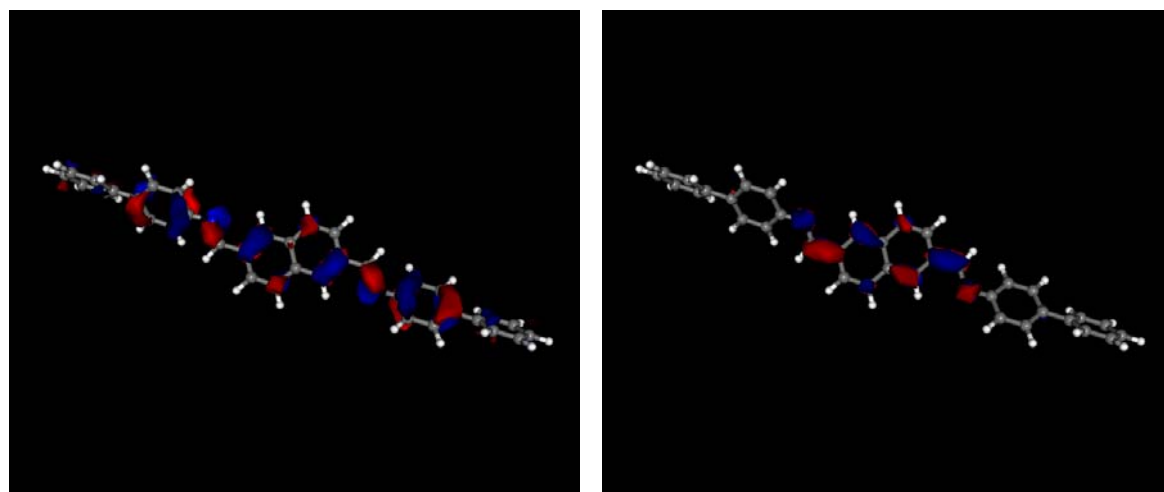


Figure S14. DFT calculation and torsion angles of the model segment of ANW 2.

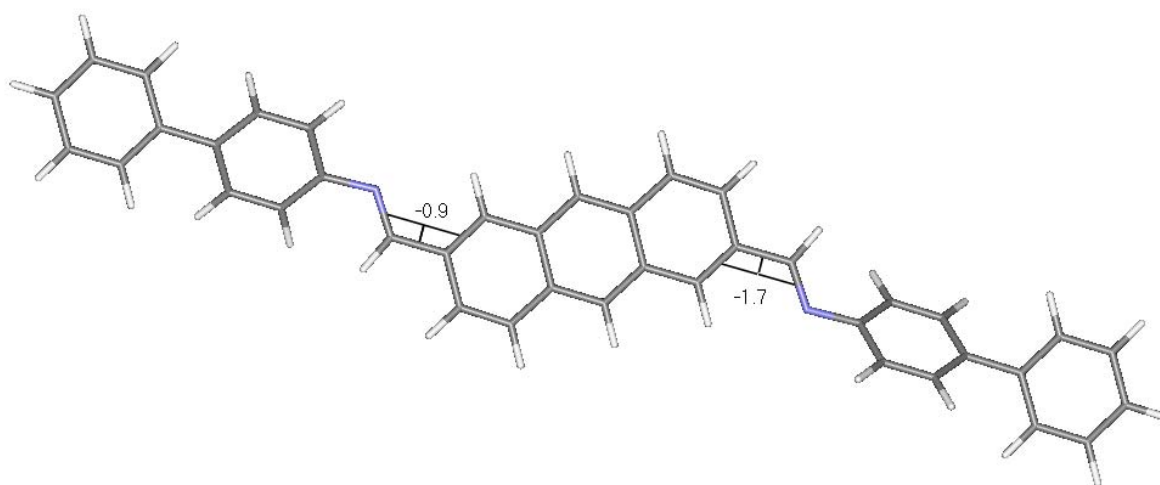


Figure S15. DFT calculation and torsion angles of the model segment of ANW 3.

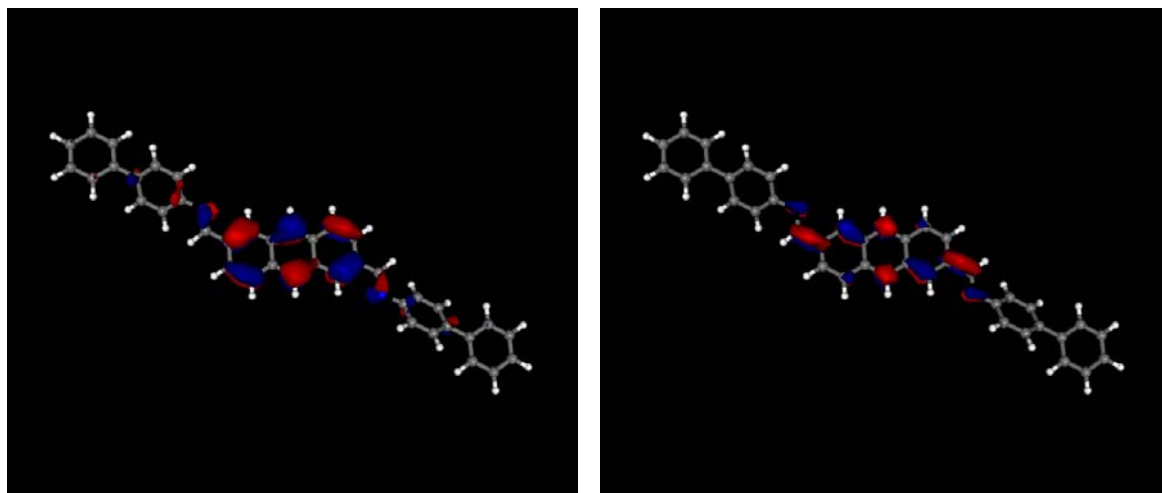


Figure S16. DFT calculation and torsion angles of the model segment of ANW 3.

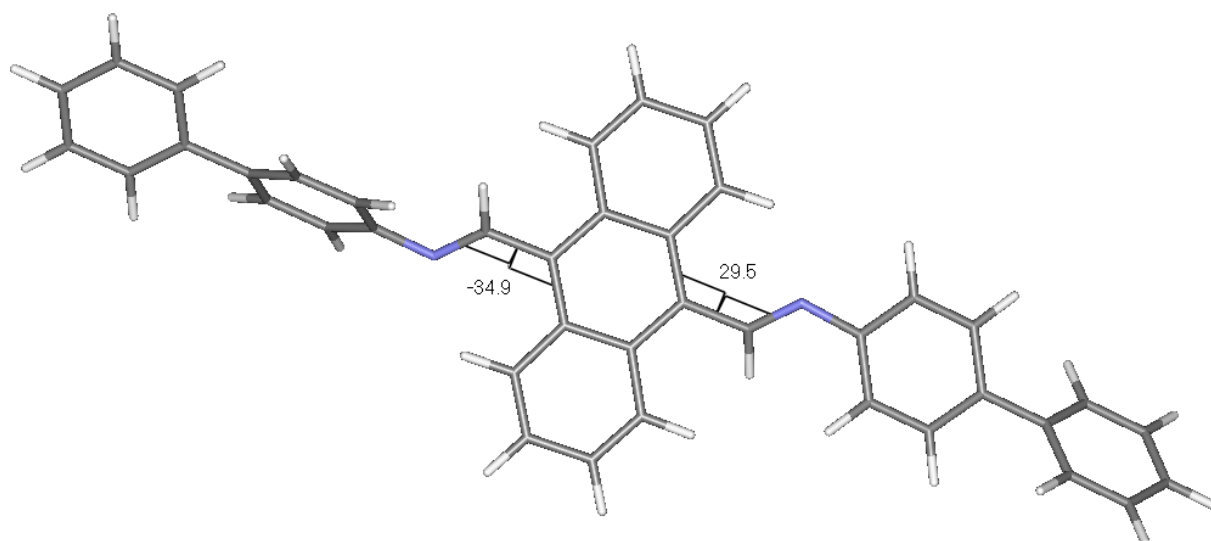


Figure S17. DFT calculation and torsion angles of the model segment of ANW 4.

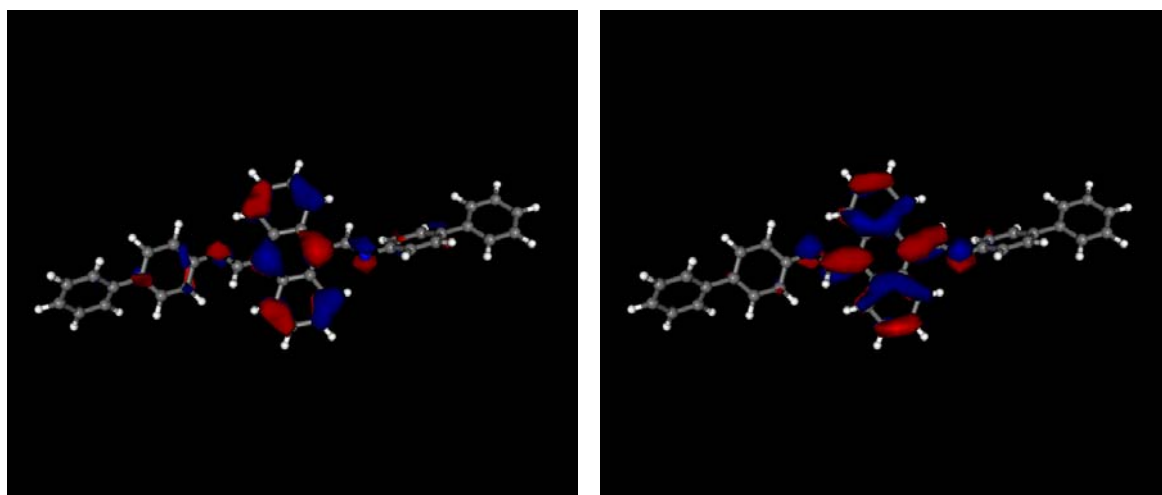


Figure S18. DFT calculation and torsion angles of the model segment of ANW 4.

Solid State UV-Vis Spectroscopy

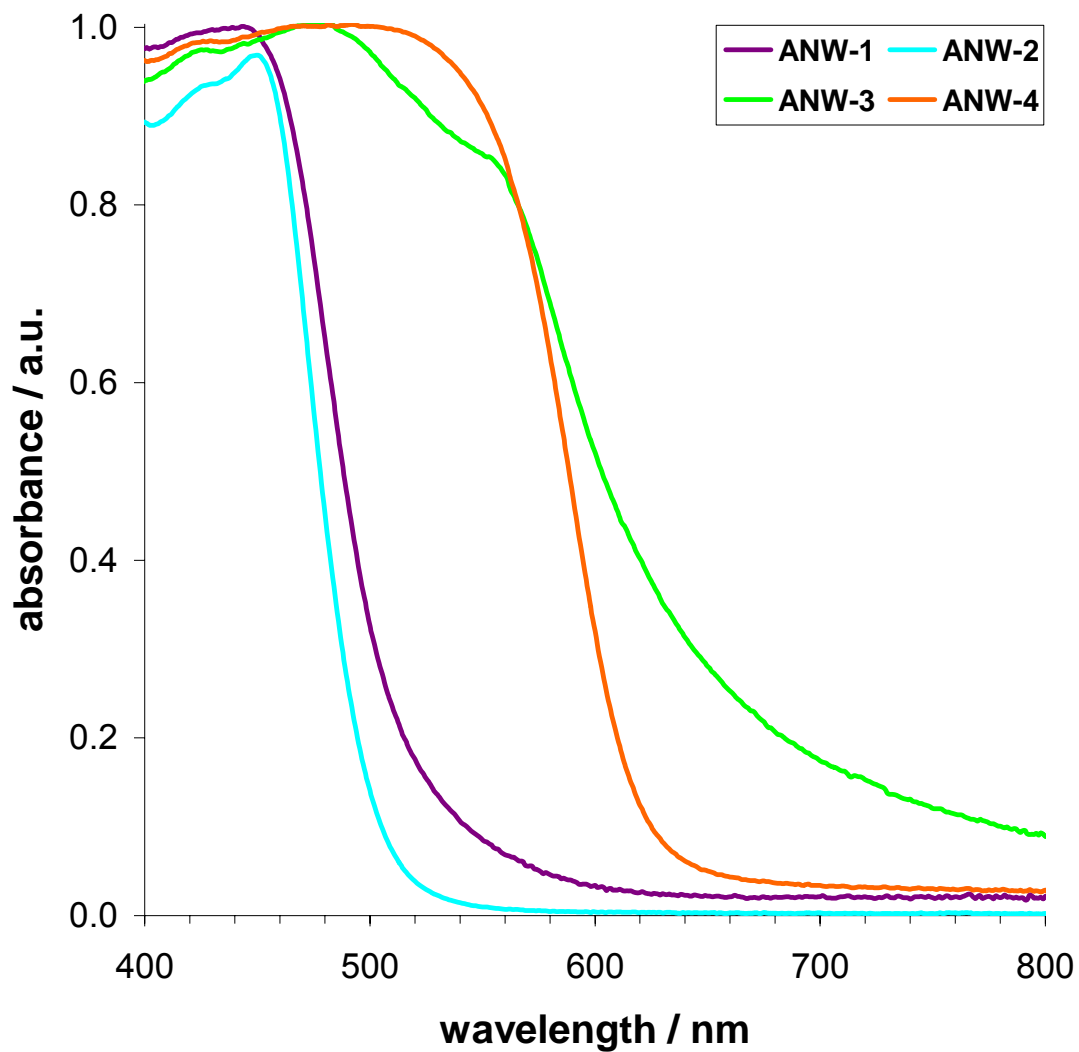


Figure S19. Solid state UV-Vis absorption spectra of the ANW networks.

Thermogravimetric Analysis

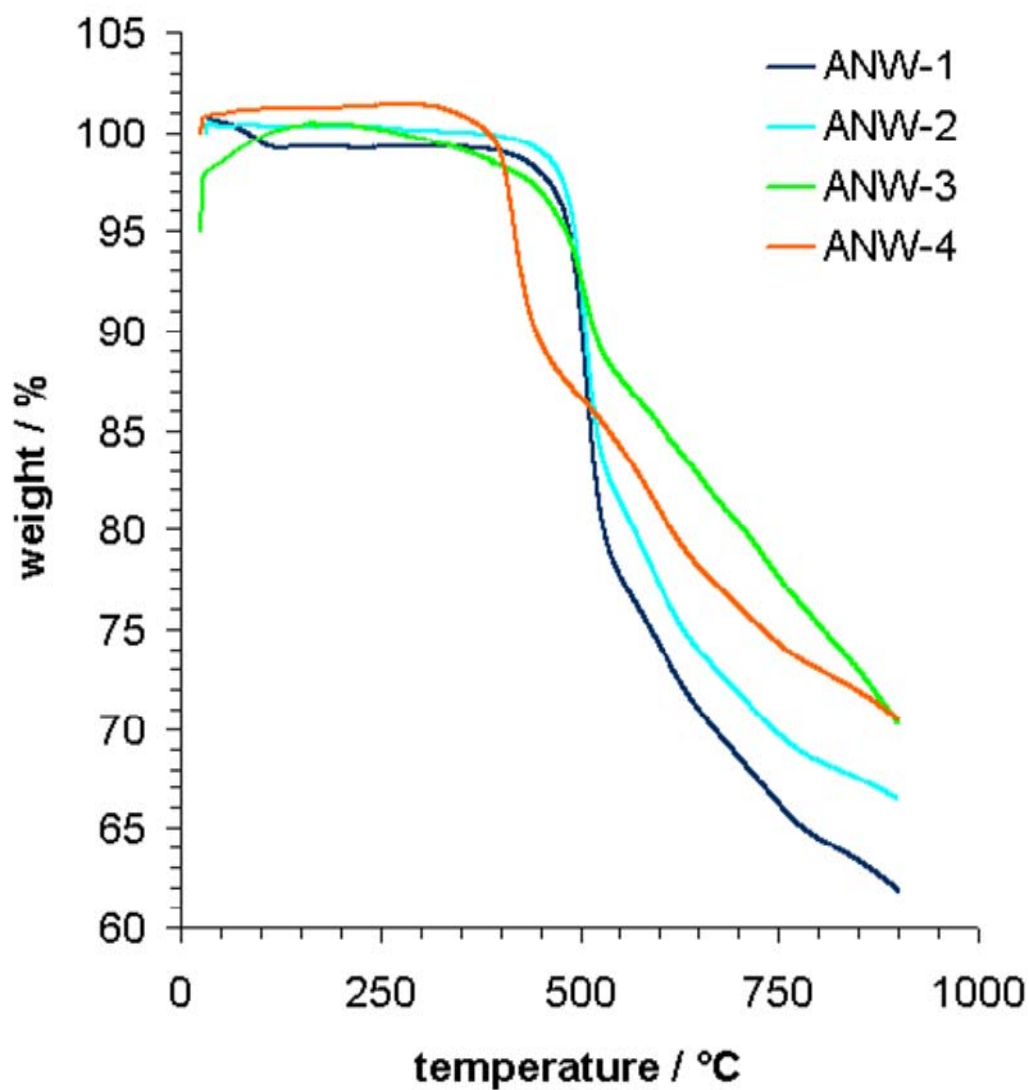


Figure S20. Thermogravimetric analysis of the ANW networks under N₂ atmosphere.

References

1. K. Hagiya, S. Mitsui and H. Taguchi, *Synthesis*, 2003, 823-828.
2. H. S. Kim, K. S. Moon and D. O. Jang, *Supramol. Chem.*, 2006, **18**, 97-101.