Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2019

Supporting Information

Supporting Information

Photo-switching and –cyclisation of Hydrogen Bonded Liquid Crystals based on Resveratrol

Meik Blanke,^{a#} Jan Balszuweit,^{a#} Marco Saccone,^{ab} Christoph Wölper,^c David Doblas Jiménez,^d Markus Mezger,^d Jens Voskuhl,^{*a} and Michael Giese^{*a}

- a. Institute of Organic Chemistry and CENIDE, University of Duisburg Essen, Universitätsstraße 7, Essen 45141, Germany. # Both authors contributed equally.
- b. Dipartimento di Ingegneria, Università degli Studi di Palermo, Viale delle Scienze, Ed. 6, Palermo 90128, Italy.
- c. Institute of Inorganic Chemistry and CENIDE, University of Duisburg Essen, Universitätsstraße 7, Essen 45141, Germany.
- d. Institut für Physik, Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, Germany.

Content

- Materials and Methods
- Synthesis of Resveratrone
- Synthesis of the hydrogen bonded complexes
- Recycling of Resveratrol
- Melting points of the starting material
- Cyclisation of hydrogen-bonded complexes
- IR-spectra
- UV-Vis spectra
- Polarized optical microscopy
- Differential scanning microscopy
- Small Angle X-Ray Scattering
- Wide Angle X-Ray Scattering
- Single-crystal X-ray analyses

- Calculations
- Literature

Materials and Methods

All commercially available solvents and compounds were used without further purification. ¹Hand ¹³C-NMR-Spectra were measured in deuterated solvents (CDCl₃, Methanol- d_4) at room temperature, using a BrukerDRX 300 or a Bruker DRX 500 (500 MHz). IR-spectra were recorded on a Bruker Alpha Platinum equipped with an ATR crystal. Absorption spectra were measured on a Jasco V-550 in acetonitrile (spectroscopic grade) in low volume quartz cuvettes. Polarized optical microscopy measurements were performed on a Nikon Eclipse Ni. The microscope is equipped with a *Linkam* heating station and an OPTIX-CAM SUMNIT 2K camera. Samples were heated and cooled with a rate of 10 °C/min. The photo-response was in situ investigated by irradiating the sample with a laser-pointer (405 nm, 5 mW). Measurements of DSC traces were performed on a Mettler Toledo DSC3+. For each sample 2 - 5 mg of substance was weighted in an aluminum crucible and heated/cooled with a rate of 10 °C/min. Argon was used as a flushing gas with a flow of 20 mL/min. All measurements were performed three times. Small (SAXS) and wide angle X-ray scattering (WAXS) measurements on hydrogen bonded LCs Reson(St-8)2, Reson(St-9)2, and Resol(St-9)3, were done at beamline P21.2 at PETRA III, DESY, Hamburg. The X-ray energy was 70.7 keV (wavelength 0.0175 nm). The samples were contained in 1 mm glass capillaries and placed in a temperaturecontrolled sample holder (Linkam HFSX350). For the sample Res_{ol}(St-9)₃ a magnetic field was applied by cylindrical neodymium permanent magnets located underneath the tip of the capillary. Scattering patterns were detected on a hybrid pixel detector (Dectris PILATUS3 X CdTe) at a sample-detector distance of 14.5 m and 1.8 m for SAXS and WAXS measurements, respectively. For Single-crystal X-ray analyses, the crystals were mounted on nylon loops in inert oil. Data of jv r s c8m were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated Mo_{Ka} radiation, $\lambda = 0.71073$ Å) at 100(2) K. Data of jv resstic8 21m were collected on a Bruker AXS D8 Venture diffractometer with Photon II detector (mono-chromated Cu_{K α} radiation, $\lambda = 1.54178$ Å, mirco-focus source) at 100(2) K.The structures were solved by Direct Methods (SHELXS-97)¹ and refined anisotropically by fullmatrix least-squares on F^2 (SHELXL-2014)^{2,3}. Absorption corrections were performed semiempirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2/3). Hydrogen atoms were refined using a riding model or rigid methyl groups. OH hydrogen atoms were refined freely.

Synthesis of Resveratrone (Reson)



2.5 liters of a 1 mmol (570 mg) solution of resveratrol in methanol was pumped with a flow of 3 mL/minute via a perestaltic pump through a photoreactor composed of a UV-transilluminator containing six 15 W 300 nm UV-tubes and a PTFE-hose grid with approximatly 4.25 m of hose directly irradiated with UV-light.

During the reaction the reactor was cooled by two fans to keep the temperature below 50 °C. After the contact time of 80 seconds the yellow and fluorescent solution was collected under argon. The whole mixture was evaporated under argon and the residue was purified by MPLC using a 120 g RP18 column and a gradient of 85/15 to 55/45 degassed water/methanol with a flow of 40 mL/minute over 5 hours. The water/methanol mixture of collected resveratrone fractions was removed by evaporation and the brown solid was purified by silica chromatography using a solvent mixture of 3:1:1:0.25 cyclohexane, dichloromethane, ethylacetate and ethanol. After evaporation 108 mg (19%) of resveratrone was received as a yellow solid. The spectroscopic parameters were in accordance with those reported before.⁴ ¹H-NMR (500 MHz, Methanol- d_4): $\delta = 8.24$ (d, J = 1.3, 1H), 7.75 (d, J = 16.2 Hz, 1H), 7.61 (dd, J = 8.7 Hz, 1.9, 1H), 7.54 (d, J = 8.7 Hz, 1H), 6.76 (d, J = 16.2 Hz, 1H), 6.64 (dt, J = 2.4 Hz, 1.2, 1H), 6.50 (d, J = 2.2 Hz, 1H), 2.38 (s, 3H) ppm. ¹³C NMR (151 MHz, Methanol- d_4) $\delta = 201.71$, 159.38, 157.12, 147.24, 138.79, 129.10, 128.01, 127.17, 125.79, 125.28, 121.43, 102.34, 102.26, 27.33 ppm.

Synthesis of Hydrogen-Bond Acceptors

St-8/9 was synthesized following a literature known procedure. Obtained ¹H-NMR spectra matched the reported ones.⁵

St-8: ¹H NMR (300 MHz, CDCl₃): $\delta = 8.54$ (d, J = 6.2 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 6.2 Hz, 2H), 7.26 (d, J = 16.3 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 16.3 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 1.86 – 1.72 (m, 2H), 1.54 – 1.21 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H). elemental analysis (%): calc. C₂₁H₂₇NO: C 81,51, H 8.79, N 4.53; found: C 81.90, H 8.76, N 4.37.

St-9: ¹H NMR (300 MHz, CDCl₃): $\delta = 8.54$ (d, J = 5.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 6.2 Hz, 2H), 7.27 (d, J = 16.3 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 16.2 Hz,

1H), 3.99 (t, J = 6.6 Hz, 2H), 1.88 – 1.72 (m, 2H), 1.37 (d, J = 54.3 Hz, 12H), 0.89 (t, J = 6.7 Hz, 3H). elemental analysis (%): calc. C₂₂H₂₉NO: C 81,69, H 9.04, N 4.33; found: C 81.60, H 9.01, N 4.37.

Ap-8/9 was synthesized following a literature known procedure. Obtained ¹H-NMR spectra matched the reported ones.⁶

Ap-8: ¹H NMR (300 MHz, CDCl₃): $\delta = 8.77$ (d, J = 6.2 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.69 (d, J = 6.2 Hz, 2H), 7.02 (d, J = 9.1 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 1.90 – 1.76 (m, 2H), 1.56 – 1.21 (m, 10H), 0.89 (d, J = 6.7 Hz, 3H). elemental analysis (%): calc. C₁₉H₂₅N₃O: C 73.28, H 8.09, N 13.49; found: C 73.60, H 7.96, N 13.50.

Ap-9: ¹H NMR (300 MHz, CDCl₃): $\delta = 8.77$ (d, J = 6.2 Hz, 2H), 7.95 (d, J = 9.1 Hz, 2H), 7.67 (d, J = 6.2 Hz, 2H), 7.02 (d, J = 9.1 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 1.92 – 1.74 (m, 2H), 1.56 – 1.20 (m, 12H), 0.89 (t, J = 6.7 Hz, 3H). elemental analysis (%): calc. C₂₀H₂₇NO: C 73,81, H 8.36, N 12.91; found: C 73.65, H 8.14, N 12.75.

Synthesis of the hydrogen-bonded complexes

 $\operatorname{Res}_{ol}(\operatorname{St-8/9},\operatorname{Ap-8/9})_3$ and $\operatorname{Res}_{on}(\operatorname{St-8/9},\operatorname{Ap-8/9})_2$ complexes were obtained by weighting resveratrol, respectively resveratrone, and 3 or 2 equivalents of the HB-Acceptor in separate vials. After dissolving both in acetone the solutions were mixed and the solvent was slowly evaporated to form the hydrogen-bonded assemblies.

Recycling of Resveratrol

The formed hydrogen-bonded complex $\text{Res}_{ol}(\text{Ap-8})_3$ was separated into Resveratrol and Ap-8 by flash column chromatography using cyclohexane:dichlormethane:ethylacetate:ethanol (3 : 1 : 0,25) with a R_f value of 0.4 for Ap-8 and a R_f value of 0.2 for Resveratrol. Regaining resveratrol allowed further conversion into resveratrone (see: Synthesis of Resveratrone (Res_{on})). After workup, the hydrogen bonded complex **Res**_{on}(Ap-8)₂ could be obtained by adding 2 eq. Ap-8 dissolved in Acetone. (see Synthesis of the hydrogen-bonded complexes).

Melting points of the starting material

ESI Table 1: melting points of the starting materials.

compound name	mp.				
Res _{ol}	253 °C (decomposition)				
Res _{on}	202 °C (decomposition)				
St- 8	92 °C				
St-9	93 °C				
Ap- 8	68 °C				
Ap-9	69 °C				

Cyclisation of hydrogen-bonded complexes



Fig S1: ¹H-NMR spectra of the hydrogen-bonded complexes after irradiation with UV-light of 300 nm prior to workup. A concentration of 0.5 mmol and an irradiation time of 80s were used.

The formation of resveratrone from the 0.5 mmol solution in Methanol over 80 s irradiation time is clearly recognizable through the signal induced by the methyl-group of resveratrone at 2.38 ppm. (see Fig S1).

The same signal with less intensity shows up in the spectra of the reaction-solutions containing St/Ap-8. The reason for the lower formation of resveratrone could be the high absorption of the UV-radiation by the compounds themselves as well as the hindrance of the intramolecular reaction due to hydrogen-bonding.

IR-spectra





Fig S3: IR spectra of the HB-assemblies $\text{Res}_{ol}(\text{St/Ap-8/9})_3$ and $\text{Res}_{on}(\text{St/Ap-8/9})_2$ are marked in black, the corresponding pure HB-Acceptor in red and the HB-Donator in blue.

UV-Vis spectra



Fig S4: Uv-vis spectra of the HB-assemblies $\text{Res}_{ol}(\text{St/Ap-8/9})_3$ and $\text{Res}_{on}(\text{St/Ap-8/9})_2$. Samples were measured in acetonitrile. Dotted lines represent the measurements of the HB-assemblies after irradiation the sample in solution with a wavelength of 365 nm for one minute.

Polarized optical microscopy



Fig S5: POM pictures taken on cooling the HB-assembly $\text{Res}_{ol}(\text{St-8})_3$ under crossed polarizers. A) isotropic state, B) nematic-phase, C) glassy state preserving the liquid-crystalline phase.

9

Supporting Information



Fig S6: POM pictures taken on cooling the HB-assembly **Res**_{ol}(**St**-9)₃ under crossed polarizers. A) isotropic state, B) nematic-phase, C) crystalline phase.



Fig S7: POM pictures taken on cooling the HB-assembly **Res**_{ol}(**Ap**-8)₃ under crossed polarizers. A) isotropic state, B) nematic-phase, C) crystalline phase.



Fig S8: POM pictures taken on cooling the HB-assembly **Res**_{ol}(**Ap**-9)₃ under crossed polarizers. A) isotropic state, B) nematic-phase, C) crystalline phase.



Fig S9: POM pictures taken on cooling the HB-assembly $\text{Res}_{on}(\text{St-8})_2$ under crossed polarizers with planar anchoring conditions. A) isotropic state, B) smectic-phase, C) glassy state preserving the liquid-crystalline phase.



Fig S9: POM pictures taken on cooling the HB-assembly $\text{Res}_{on}(\text{St-9})_2$ under crossed polarizers with planar anchoring conditions. A) isotropic state, B) smectic-phase.



Fig S10: POM pictures taken on cooling the HB-assembly **Res**_{on}(**Ap**-8)₂ under crossed polarizers with planar anchoring conditions. A) isotropic state, B) smectic-phase.



Fig S11: POM pictures taken on cooling the HB-assembly **Res**_{on}(**Ap**-9)₂ under crossed polarizers. A) isotropic state, B) smectic-phase.

Differential scanning calometry



Fig S12: DSC profile of the HB-assembly Res_{ol}(St-8)₃ measured with a heating/cooling rate of 10 °C/min.

10 mW	Integral -52,25 mJ Integral normalized -23,02 Jg^-1 normalized Onset 43,08 °C Onset Peak 49,20 °C Peak Heating Rate 10,00 °Cmin^-1 Heating Rate	51,37 mJ Integral 22,63 Jg^-1 normalized 69,98 °C Onset 78,62 °C Peak 10,00 °Cmin^-1 Heating Rate	10,98 mJ 4,84 Jg^-1 136,76 ℃ 138,26 ℃ 10,00 ℃Cmin^-1
•		Integral normalized Onset Peak Heating Rate	-10,42 mJ -4,59 Jg^-1 138,83 ℃ 137,90 ℃ -10,00 ℃min^-1

Fig S13: DSC profile of the HB-assembly $Res_{ol}(St-9)_3$ measured with a heating/cooling rate of 10 °C/min.

125 130

 155 °C



Fig S14: DSC profile of the HB-assembly $\text{Res}_{ol}(\text{Ap-8})_3$ measured with a heating/cooling rate of 10 °C/min.



Fig S15: DSC profile of the HB-assembly $\text{Res}_{ol}(\text{Ap-9})_3$ measured with a heating/cooling rate of 10 °C/min.



Fig S16: DSC profile of the HB-assembly $\text{Res}_{on}(\text{St-8})_2$ measured with a heating/cooling rate of 10 °C/min.



Fig S17: DSC profile of the HB-assembly $\text{Res}_{on}(\text{St-9})_2$ measured with a heating/cooling rate of 10 °C/min.



Fig S18: DSC profile of the HB-assembly $\text{Res}_{on}(Ap-8)_2$ measured with a heating/cooling rate of 10 °C/min.



Fig S19: DSC profile of the HB-assembly $\text{Res}_{on}(\text{Ap-9})_2$ measured with a heating/cooling rate of 10 °C/min.



Small Anlge X-Ray Scattering

Fig S20: SAXS pattern of LC **Res**_{on}(**St**-8)₂ at 115 °C. (upper left) Full 2D detector image with 172 μ m pixel size. (upper right) Average of the 4 vertically and horizontally flipped quadrants. (bottom) Radial average of the scattering pattern with real space periodicity $d = 2\pi / q_{\text{max}}$ corresponding to the observed scattering peak.



Fig S21: SAXS pattern of LC **Res**_{ol}(**St**-9)₃ at 95 °C. (upper left) Full 2D detector image with 172 μ m pixel size. (upper right) Average of the 4 vertically and horizontally flipped quadrants. (bottom) Radial average of the scattering pattern with real space periodicity $d = 2\pi / q_{\text{max}}$ corresponding to the observed scattering peak.



Fig S22: SAXS pattern of LC $\operatorname{Res}_{on}(\operatorname{St-9})_2$ at 127 °C. (upper left) Full 2D detector image with 172 µm pixel size. (upper right) Average of the 4 vertically and horizontally flipped quadrants. (bottom) Radial average of the scattering pattern with real space periodicity $d = 2\pi / q_{\text{max}}$ corresponding to the observed scattering peak.



Wide Angle X-Ray Scattering

Fig S23: WAXS pattern of LC $\text{Res}_{on}(\text{St-8})_2$ at 115 °C. (upper left) Full 2D detector image with 172 μ m pixel size. (upper right) Average of the 4 vertically and horizontally flipped quadrants. (bottom) Radial average of the scattering pattern with real space periodicity $d = 2\pi / q_{\text{max}}$ corresponding to the observed scattering peak.





Fig S24: WAXS pattern of LC **Res**_{ol}(**St**-9)₃ at 95 °C. (upper left) Full 2D detector image with 172 μ m pixel size. (upper right) Average of the 4 vertically and horizontally flipped quadrants. (bottom) Radial average of the scattering pattern with real space periodicity $d = 2\pi / q_{\text{max}}$ corresponding to the observed scattering peak.



Fig S25 WAXS pattern of LC $\operatorname{Res}_{on}(\operatorname{St-9})_2$ at 127 °C. (upper left) Full 2D detector image with 172 µm pixel size. (upper right) Average of the 4 vertically and horizontally flipped quadrants. (bottom) Radial average of the scattering pattern with real space periodicity $d = 2\pi / q_{\text{max}}$ corresponding to the observed scattering peak.

Single-crystal X-ray analyses.



Fig S26: Molecular structure of Res_{ol} (St-8)₃.



Fig S27: Molecular structure of Res_{on}(St-8)₂.

Identification code	Res _{ol} (St-8) ₃	Reson(St-8)2
Empirical formula	C ₇₇ H ₉₃ N ₃ O ₆	C ₅₆ H ₆₆ N ₂ O ₅
CCDC number	1939466	1939467
М	1156.54	847.10
Crystal size [mm]	$0.491 \times 0.188 \times 0.150$	$0.240 \times 0.230 \times 0.058$
<i>T</i> [K]	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	<i>P</i> -1
<i>a</i> [Å]	22.357(3)	9.8815(13)
<i>b</i> [Å]	10.0540(15)	13.0611(16)
<i>c</i> [Å]	28.899(4)	19.081(3)
α [°]	90	80.647(6)
β[°]	91.602(8)	83.990(6)
γ [°]	90	79.057(6)
<i>V</i> [Å ³]	6493.2(17)	2378.8(5)
Ζ	4	2
$D_{\text{calc}} [g \cdot \text{cm}^{-3}]$	1.183	1.183
μ (Mo/Cu K_{α} [mm ⁻¹])	0.074	0.584
Transmissions	0.75/0.71	0.75/0.62
F(000)	2496	912
Index ranges	$-34 \le h \le 34$	$-12 \le h \le 12$
	$-14 \le k \le 15$	$-15 \le k \le 16$
	$-43 \le l \le 42$	$-24 \le l \le 24$

θ_{\max} [°]	33.211	82.299
Reflections collected	210866	164209
Independent reflections	24524	10220
R _{int}	0.0413	0.0610
Refined parameters	790	579
$R_1 \left[I > 2\sigma(I) \right]$	0.0516	0.0596
wR_2 [all data]	0.1428	0.1394
<i>x</i> (Flack)		
GooF	1.043	1.096
$\Delta \rho_{\text{final}} (\text{max/min}) [\text{e} \cdot \text{Å}^{-3}]$	0.619/-0.326	0.253/-0.342

Calculations

Calculations were performed on a pc equipped with an Intel® CoreTM i5-7400 Processor and 8 GB RAM and the *CrystalExplorer* program. The model energies were calculated using the option "accurate". A cluster of molecules within a radius of 3.8 Å from the reference molecule was considered.

See http://130.95.176.70/wiki/index.php/Intermolecular_Interaction_Energies for further details.

Details on Structure Determinants

Below we give a chart which explain the information given in the ESI Table 1 and 2.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	2	3	4	5	6	7	8	9	10

1) Structure Determinant color, as provided in Fig. S20 and S21

2) The number of pairs, N, in the graphics window with that energy.

- 3) Symmetry operator joining the two molecules in the pair.
- 4) Distance between centers of mass of both molecules (Å).
- 5) Level of theory at which the electron density is computed: B3LYP/6-31G(d,p) here.
- 6) Electrostatic contribution (kJ/mol).

7) Polarization contribution (kJ/mol).

8) Dispersion contribution (kJ/mol).

9) Repulsion contribution (kJ/mol).

10) Total energy (kJ/mol): This is the *sum of scaled components* (using the scale factors appropriate to the model as given below), but the *separate components are not scaled*.

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP B3LYP/6-31G(d,p) electron	1.057	0.740	0.871	0.618

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-	6.84	B3LYP/6-31G(d,p)	-6.3	-1.9	-41.5	18.7	-32.6
1	-	17.51	B3LYP/6-31G(d,p)	-68.9	-16.6	-10.5	82.7	-43.2
1	-	5.08	B3LYP/6-31G(d,p)	-15.1	-3.0	-47.4	34.1	-38.4
1	-	6.19	B3LYP/6-31G(d,p)	-8.7	-1.9	-32.6	20.9	-26.1
1	-	16.42	B3LYP/6-31G(d,p)	-73.8	-18.3	-12.3	91.7	-45.6
1	-	15.65	B3LYP/6-31G(d,p)	-65.1	-16.3	-14.5	80.5	-43.9

ESI Table 3 Res_{ol}(St-8)₃ energy decomposition

ESI Table 4 $Res_{on}(St-8)_3$ energy decomposition

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
a	1	-	7.70	B3LYP/6-31G(d,p)	-6.4	-2.3	-50.8	34.3	-31.5
	1	-	16.31	B3LYP/6-31G(d,p)	-75.5	-19.3	-12.5	92.4	-47.9
	1	-	6.18	B3LYP/6-31G(d,p)	-13.5	-2.7	-63.2	42.3	-45.2
	1	-	7.41	B3LYP/6-31G(d,p)	-3.6	-1.5	-21.3	8.1	-18.5
	1	-	15.02	B3LYP/6-31G(d,p)	-73.7	-18.8	-14.6	83.8	-52.8
	1	-	10.42	B3LYP/6-31G(d,p)	-16.4	-5.0	-21.0	25.7	-23.4



Structure Determinant 5 32.6 kJ/ mol



Structure Determinant 6 26.1 KJ/ Mol

Fig S28: Supramolecular hierarchy of the six most stabilizing interactions in the $\text{Res}_{ol}(\text{St-8})_3$ structure as provided by CrystalExplorer. Cyan-colored lines represent short intermolecular contacts below the sum of the van der Waals radii of the respective atoms. Colour chart: C, grey, H, white, O, red, N, purple.



Structure Determinant 1 52.8 kJ/mol



Structure Determinant 3 45.2 kJ/mol



Structure Determinant 5 23.4 kJ/mol

Structure Determinant 2 47.9 kJ/mol



Structure Determinant 4 31.5 kJ/mol



Structure Determinant 6 18.5 kJ/mol

Fig S29: Supramolecular hierarchy of the six most stabilizing interactions in the $\text{Res}_{on}(\text{St-8})_3$ structure as provided by CrystalExplorer. Cyan-colored lines represent short intermolecular contacts below the sum of the van der Waals radii of the respective atoms. Colour chart: C, grey, H, white, O, red, N, purple.

Literature

[1] G. M. Sheldrick, Acta Crystallogr. 1990, A46, 467.

[2] G. M. Sheldrick, SHELXL-2014, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) 2014 (see also: Sheldrick, G. M. *Acta Cryst.* 2008, A64, 112).

[3] shelXle, *A Qt GUI for SHELXL*, C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* 2011, **44**, 1281-1284.

[4] I. Yang, E. Kim, J. Kang, H. Han, S. Sul, S. B. Park and S. K. Kim, *Chem. Commun.* 2012, 48, 3839-3841.

[5] M. Giese, T. Krappitz, R. Y. Dong, C. A. Michal, W. Y. Hamad, B. O. Patrick and M. J. MacLachlan, J. Mater. Chem. C 2015, 3, 1537–1545.

[6] M. Pfletscher, C. Wölper, J. S. Gutmann, M. Mezger and M. Giese, *Chem. Commun* 2016, 52, 8549–8552.