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Research paper

A novel approach to achieve molecular switching in solid-state driving by thermal treatment: A photochromic zinc-coordination polymer



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ABSTRACT

The molecular switching of complexes based on diarylethenes in a solid-state is their most frequently studied property. This switching becomes possible when the active carbon atoms acquire a suitable interatomic separation in the molecule. Even if the structural analysis may suggest conditions disfavouring the occurrence of such switching, it may still be enabled by post-synthetic modification of the sample, like dehydration. In the present study, a novel one-dimensional coordination polymer with composition $\{[Zn(\mu_3-HA)(H_2O)_3]\cdot H_2O\}_n$ (*I*) was prepared and characterized. In its solid state, however, its thiophene rings were arranged in the nonswitchable conformation yielding a C--C separation 4.148(6) Å between the active carbon atoms. After fully dehydrating the sample, this interatomic separation decreased to 3.814 Å, making it susceptible to photochromism by UV radiation.

1. Introduction

In general, photochromism is defined as a reversible transformation two isomers having different absorption spectra induced in one or both directions by photoirradiation. Photochromic compounds have attracted remarkable attention because of their potential applicability in optical memory media, optical switching devices and as control elements in molecular motors [1,2].

Among them, diarylethenes with heterocyclic aryl groups are the most promising compounds for application, due to their resistance against fatigue and their thermally irreversible photochromic properties. Moreover, it has been recently found that some diarylcyclopentenes derivatives with thiophene or benzothiophene rings undergo photochromic reactions even in the single-crystalline phase [3–5]. Upon irradiation with UV light, diarylethene molecules undergo photocyclization and this reaction is accompanied by the colour change that is dependent on the chemical structure of the molecules. Upon irradiation with visible light, the closed coloured form turns to the initial colourless open form and this process can be repeated many times. Photocyclization is a reversible process and can be observed in solution and rarely in solid-state, because in crystals large geometrical structure changes are prohibited. However, with metal cations coordinated at both ends of the diarylethene switch aryl groups, the interaction

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between the metallic ions can be switched by photo-irradiation, because the π -conjugated bond structures between the two aryl groups are different in the two isomers. Based on published results it has been shown that in the case of diarylethenes, the distance between the active carbon atoms should be within 3.45–3.80 Å [6–8].

In the present work, we report the synthesis and characterization of one-dimensional coordination polymer with composition {[Zn(μ_3 -HA) (H₂O)₃]·H₂O}_n (*I*, HA = 1,2-bis(5-carboxy-2-methylthien-3-yl)cyclopentene) and its photochromic reaction in solid-state before and after dehydration process. It was shown, that after the dehydration process of the sample, the interatomic C···C separation decreased from the original value of 4.148 to 3.814 Å, making it susceptible to photochromism by UV radiation.

2. Experimental

2.1. Materials

Zinc(II) nitrate tetrahydrate and chemicals used in the synthesis of 1,2-bis(5-carboxy-2-methylthien-3-yl)cyclopentene (HA) were purchased from Sigma-Aldrich or Acros Organics and used without further purification.



2.2. Synthesis

2.2.1. Synthesis of 1,2-bis(5-carboxy-2-methylthien-3-yl)cyclopentene (HA)

2.2.1.1. 2-Chloro-5-methylthiophene (1). 2-methylthiophene (50 ml, 0.52 mol) and N-chlorosuccinimide (76 g, 0.57 mol) were added to a stirred solution of benzene (200 ml) and glacial acetic acid (200 ml). The suspension was stirred for 30 min at room temperature, then heated to reflux for 1 h. The cooled mixture was poured into 3 M NaOH solution (300 ml). The organic phase was washed with a solution of 3 M NaOH (3×200 ml), dried with Na₂SO₄, filtered and the solvent was evaporated in vacuum to yield a light yellow liquid. The final product was purified by vacuum distillation at pressure 50 mbar and 70 °C to give a colourless liquid (57.65 g, 84%). ¹H NMR (400 MHz, CDCl₃): δ 2.30 (s, 3H, H(3)), 6.40–6.41 (m, 1H, H(2)), 6.58 (d, J = 3.6 Hz, 1H, H (1)) ppm. Corresponding ¹H NMR spectrum of 1 with assignments of hydrogen atoms is depicted in Fig. S1 in ESI.

2.2.1.2. 1,2-bis(5-chloro-2-methylthien-3-yl)pentane-1,5-dione (2). To a stirred solution of glutaryldichloride (12.08 g, 71.5 mmol) and 2-chloro-5-methylthiophene (1, 18.84 g, 142 mmol) in CH₂Cl₂ (150 ml) in ice bath, AlCl₃ (22.88 g, 172 mmol) was carefully added. After addition of AlCl₃, the reaction mixture was stirred for 2 h at room temperature. Then 50 ml of water was added to the reaction mixture and extracted with CH₂Cl₂ (3 × 150 ml). The combined organic phases were washed with water (2 × 100 ml), dried with Na₂SO₄, filtered off and the solvent was evaporated in vacuum to yield a brown tar (25.35 g, 98%). ¹H NMR (400 MHz, CDCl₃): δ 2.06 (p, *J* = 6.9 Hz, 2H, H(3)), 2.66 (s, 6H, H(4)), 2.86 (t, *J* = 6.9 Hz, 4H, H(2)), 7.18 (s, 2H, H(1)) ppm. Corresponding ¹H NMR spectrum of **2** with assignments of hydrogen atoms is depicted in Fig. S2 in ESI.

2.2.1.3. 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene (3). In a threeneck flask, zinc powder (10 g, 153 mmol) was added to anhydrous THF (200 ml) under nitrogen atmosphere. Afterwards, TiCl₄ (11.85 ml, 108 mmol) was added to this suspension very carefully using a syringe with needle (!be careful!) and the solution was refluxed for 1 h. In the next reaction step, the mixture was cooled in an ice bath and 1,2-bis(5chloro-2-methylthien-3-yl)pentane-1,5-dione (2) (25.35 g, 70 mmol) was added. The final mixture was refluxed for 2 h. The reaction mixture was then cooled down, 200 ml 10% aq. K₂CO₃ was added and then it was extracted with Et₂O (3 imes 200 ml). The combined organic phases were dried with Na₂SO₄, filtered off and evaporated under vacuum to yield a brown tar. After purification by column chromatography on silica gel (mobile phase: petroleum ether 40-60) a slightly yellow crystalline solid was obtained (16.43 g, 71%). ¹H NMR (400 MHz, $CDCl_3$): δ 1.90 (s, 6H, H(4)), 2.03 (p, J = 7.5 Hz, 2H, H(1)), 2.73 (t, J = 7.5 Hz, 4H, H(2)), 6.56 (s, 2H, H(3)) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ 14.1 (C(8)), 22.8 (C(1)), 28.1 (C(2)), 123.2 (C(6)), 126.6 (C(5)), 133.3 (C(4)), 134.4 (C(3)), 134.8 (C(7)) ppm. Corresponding ¹H and ¹³C NMR spectra of **3** with assignments of hydrogen and carbon atoms are depicted in Fig. S3 in ESI.

2.2.1.4. 1,2-bis(5-carboxy-2-methylthien-3-yl)cyclopentene (4). 3 (9 g, 27.3 mmol) was dissolved in dry THF (100 ml) under nitrogen atmosphere. To this solution, *n*-butyllithium (43.2 ml of a 1.6 M solution in hexane, 69 mmol) was added dropwise at room temperature while stirring. A brown precipitate of the organyl lithium salt was formed. Then solid CO_2 was added into the mixture to give a colourless precipitate of the lithium salt of **7**. Then the solution was allowed to warm up to room temperature and consequently quenched with an aqueous solution of NaOH (10 wt%, 150 ml). The water layer was washed with diethyl ether (3 × 50 ml) and then acidified with conc. HCl until pH = 1 was reached. The precipitate was collected and recrystallized from 300 ml (methanol:diethyl ether /1:4/ v:v) to yield (7.28 g, 76%) as a slightly brown powder. ¹H NMR

(400 MHz, CDCl₃): δ 1.92 (s, 6H), 2.01 (p, J = 7.5 Hz, 2H), 2.77 (t, J = 7.5 Hz, 4H), 7.42 (s, 2H) ppm. ¹³C NMR (100.6 MHz, DMSO- d_6): δ 14.3, 22.2, 37.8, 130.4, 133.8, 134.2, 136.3, 141.6, 162.5 ppm. Corresponding ¹H and ¹³C NMR spectra of **4** with assignments of hydrogen and carbon atoms are depicted in Fig. S4 in ESI.

2.2.2. Synthesis of $\{[Zn(\mu_3-HA)(H_2O)_3] \cdot H_2O\}_n$ (I)

150 mg (0.57 mmol) of Zn(NO₃)₂·4H₂O and 50 mg (0.14 mmol) of H₂HA were added to 20 ml of distilled water. For deprotonation of dicarboxylic acid 2.8 cm³ of 0.1 M NaOH (0.28 mmol) solution was added to the reaction mixture. The reaction mixture was refluxed for 3.5 h and after cooling to the laboratory temperature, the solution was left for isothermal crystallization for two weeks. During this time, colourless crystals of *I* were formed (see Fig. S3 in ESI), which were filtered off, washed with water and dried in a stream of air (yield: 48 mg, 71% based on H₂HA). EA (485.89 g.mol⁻¹) and FAAS, clcd: C 42.02%; H 4.98%; S 13.20%; Zn 13.46%; found: C 41.54%; 4.84%; S 13.04%; Zn 13.75%.

2.3. Methods and characterization

The elemental analysis was performed with CHNOS Elemental Analyzer vario MICRO from Elementar Analysensysteme GmbH with a mass sample approximately 3 mg.

The determination of the amount of zinc(II) ions in compound I have conducted on AAS PERKIN-ELMER 410 at wavelength 214 nm. Before measurement, the sample was mineralized in aqua regia upon heating.

¹H NMR and ¹³C NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer at a frequency of magnetic field 400 (¹H NMR) and 100 (¹³C NMR) MHz, respectively using TMS as the internal reference. Samples were dissolved in CDCl₃ or DMSO- d_6 solvents.

Infrared spectra were recorded with Avatar FT-IR 6700 spectrometer in the wavenumber range 4000–650 cm^{-1} using ATR (attenuated total reflectance) technique.

The TG measurement was carried out using a TGA Q500 instrument under dynamic conditions with a heating rate of 10 °C.min⁻¹. The sample has been heated under air atmosphere with an air flow rate of 50 cm³.min⁻¹ in the temperature range from 30 to 800 °C.

The crystallinity of the sample *I* before and after dehydration process was determined by PXRD measurements on a Bruker AXS D8 ADVANCE diffractometer in the Bragg–Brentano geometry using CuK α ($\lambda = 1.54056$ Å) radiation with a NaI dynamic scintillation detector (Vantec-1) in the 2 θ range of 2-30°. In order to achieve parallel and clean X-ray beam for PXRD experiments, initially divergent CuK α radiation emitted from X-ray lamp was further guided through the multi-layered mirror and set of slits.

UV/VIS measurements of the free ligand in methanol and compound I and \hat{I} in solid-state were performed on SPECORD 250 spectrometer by Analytic Jena. As a source of ultraviolet and visible light for switching experiments in solution and solid-state 6 W UV/VIS lamp by KRÜSS Optronic with wavelengths, 256/578 nm was used.

DFT computations have been carried out using Gaussian 16, Revision A.03. Computations employed the M11 functional and the 6-31 + G(d,p) basis set for all atoms [9]. The Hessians for geometry optimizations were estimated before the initial step of optimizations. Geometry optimizations were performed using redundant internal coordinates with all coordinates free to vary.

Diffraction data for *I* were collected at 150 K using graphite monochromated MoK_{α} radiation on Nonius KappaCCD diffractometer equipped with a Bruker APEX-II detector. The phase problem was solved by intrinsic phasing and the structure model was refined by full-matrix squares on F^2 using the SHELX program package [10]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon atoms were refined with no positional constraints. All hydrogen

atoms were refined with isotropic thermal parameters fixed to $1.2U_{eq}$ of their parent atoms. Crystal data for { $[Zn(\mu_3-HA)(H_2O)_3] \cdot H_2O\}_n$, CCDC 1491694, colourless block, crystal size: $0.29 \times 0.14 \times 0.05 \text{ mm}^3$, monoclinic crystal system, space group $P_{2_1/c}$, a = 20.333(3) Å, b = 10.3696(14) Å, c = 9.3867(11) Å, $\beta = 99.726(3)^\circ$, V = 1950.7(4) Å³, Z = 4, $D_c = 1.647 \text{ g.cm}^{-3}$, $\mu = 1.516 \text{ mm}^{-1}$, Goodness of Fit (GooF) = 0.993. Of 14,460 total reflections collected (-24 $\leq h \leq 25$, $-12 \leq k \leq 12$, $-11 \leq l \leq 11$), 3819 were unique. Based on these data $R_1/R_{1,all}$ ($w_{R2}/w_{R2,all}$) = 0.0532/0.1041 (0.0876/0.1174) for 275 parameters. Structure figures were drawn using DIAMOND 3.0 [11].

3. Results and discussion

3.1. Synthesis

The H₂HA ligand was prepared by modification of organic synthetic procedures described in [12–14]. In the first step, chlorination of 2-methyltiophene was followed by Friedel-Crafts acylation with glutaryldichloride and using AlCl₃ as a catalyst. The cyclization reaction with TiCl₄ led to the formation of a cyclopentene ring. The final dicarboxylic acid was prepared by substituting the chlorine atoms using *n*-BuLi and CO₂, then followed by acidification. ¹H and ¹³C NMR spectra of the final product used further as a ligand for the synthesis of *I*, together with the assignment of hydrogen and carbon atoms are depicted in Fig. 1b.

Compound I was prepared by isothermal crystallization using zinc nitrate tetrahydrate, H₂HA as the ligand and NaOH in a 4:1:2 M ratio.

After two weeks (in darkness), colourless crystals were formed, which were further characterized and their photochromic properties studied.

3.2. Crystal structure of $\{[Zn(\mu_3-HA)(H_2O)_3]\cdot H_2O\}_n$

A view of the structural model is shown in Fig. 2a, selected bond distances and angles are summarized in Table S1 in ESI. The compound crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. The asymmetric unit is built from one zinc(II) ion, one HA ligand, three coordinated and one crystallization water molecules. The Zn(II) ions are hexacoordinated with donor set [ZnO₆] and the coordination polyhedron can be described as a distorted tetragonal bipyramid. The equatorial plane of tetragonal bipyramid is formed by four Zn-O bonds with lengths in the range of 1.986(3)–2.187(4) Å, (O2, O4, O5, O7) and axial positions are occupied by two oxygen atoms O1 and O3. The tetragonal bipyramid is distorted with the angle O1_{ax}-Zn-O3_{ax} 171.32(13)°, deviating slightly from the ideal octahedral 180°. Both carboxylic groups of the H₂HA ligand are deprotonated and coordinated to zinc(II) ions in different coordination fashion. The carboxylate group including C16 is coordinated in a monodentate mode, the carboxylate group including C1 in syn-anti mode and thus one HA linker bridges three central atoms (μ_3 -bridge).

Compound I can be included into the group of coordination polymers and exhibits a chain-like structure propagating parallel with the c crystallographic axis. The 1D polymeric chains are stabilized on one side by hydrophobic effects formed between the cyclopentene rings of



Fig. 1. Preparation of H₂HA ligand (1,2-bis(5-carboxy-2-methylthien-3-yl)cyclopentene): (1) NCS, reflux, benzene, acetic acid, 84%; (2) glutaryldichloride, AlCl₃, CH₂Cl₂, 98%; (3) Zn, TiCl₄, reflux, THF, 71%; (4) *n*-BuLi, CO₂ (s), RT, THF, 76%.



Fig. 2. a) Coordination environment of Zn(II) ion and coordination modes of HA ligand. b) A view showing final crystal packing of 1D polymeric chains, which are stabilized by hydrogen bonds formed between water molecules and hydrophobic effect of cyclopentene rings.

the HA ligands (hydrophobic part in Fig. 2b) and by several weak and medium hydrogen bonds formed between coordinated and crystallization water molecules (hydrophilic part in Fig. 2b) on the other. The list of intermolecular hydrogen bonds is summarized in Table S2 in ESI. The distance between reactive carbons of HA ligand in *I* is 4.148(2) Å, sufficiently long to interact in solid-state. Based on literature data, an effective C···C distance for UV driven photochromism ranges from 3.45 Å to 3.80 Å [6–8].

3.3. Infrared spectroscopy

IR spectroscopy confirms the presence of HA ligand and water molecules in *I* (see Table S3 and Fig. S5 in ESI). The presence of coordinated and crystallization water molecules is evident from the broad absorption band located at 3428 cm⁻¹ corresponding to ν (OH) stretching vibration. At lower wavenumbers, the presence of HA molecules is evident from several weak absorption bands appearing below 3000 cm⁻¹, which correspond to the stretching vibrations of CH₂/CH₃ groups. The absence of a strong absorption band at 1660 cm⁻¹ corresponding to ν (C=O) vibration of the carboxylic group of the free HA indicates complete deprotonation of HA carboxyl groups during the synthesis. The band of antisymmetric carboxylate stretch, v_{as} (COO⁻) was found at 1564 and 1555 cm⁻¹, the band of symmetric v_s (COO⁻) was observed at 795 cm⁻¹, respectively.

3.4. Study of thermal robustness

For the investigation of thermal robustness and the dehydration process of the synthesized polymer, thermal analysis was conducted in an air atmosphere (see Fig. S6 in ESI). Compound *I* is thermally stable up to 60 °C; above this temperature in the range 60–155 °C dehydration takes place in two decomposition steps. In this temperature range, a total mass loss of 14.2% was observed, corresponding to the release of four water molecules (clcd. mass loss 14.8%). The observed decomposition step could be separated into two distinct processes: the first one in temperature range 70–110 °C (mass loss obs. 7.2%, clcd. 7.4%) corresponding to the release of two water molecules, then the second in range 110–155 °C (mass loss obs. 7.0%, clcd. 7.4%) corresponding also to the release of another two water molecules. The dehydrated form (*Í*) is thermally stable in the temperature range 155–240 °C, which was

deduced from a plateau appearing on the TG curve (see Fig. S6 in ESI). At higher temperatures, the decomposition of $\{[Zn(HA)]\}_n$ chains takes place in several overlapping steps. The final product of thermal decomposition was ZnO (obs. residual mass 18.4%, clcd. residual mass 17.8%). All observed decomposition steps and mass changes are in good agreement with the crystal structure and the chemical composition of *I*.

3.5. Powder X-ray diffraction measurements

Based on TG measurement it was possible to determine the dehydration temperature of compound *I*. The phase purity of as-synthesized and dehydrated material was studied by powder X-ray diffraction (PXRD) experiments. Fig. S7 in ESI shows a comparison of the experimental PXRD pattern of *I* and the pattern calculated from the singlecrystal X-ray data. Very good agreement between the measured and simulated pattern was observed, indicating the presence of pure phase of *I*. Differences observed in the diffraction line intensities can be attributed to the variation of the preferred orientation of crystallites in the powdered as-synthesized sample. The pattern of the dehydrated compound demonstrates, that the crystal structure of the compound does not collapse after removal of the solvent molecules and a formation of novel phase was observed.

3.6. Photochromic properties

Initially, the switching properties of the free ligand were investigated in its methanol solution (0.575 µmol.dm⁻³ concentration) and the corresponding time-dependent spectra after irradiation at 254 nm are depicted in Fig. 3. Before irradiation, the colourless solution of H₂HA had no absorption in the visible region and exhibited a single intensive band at 256 nm corresponding to $\pi \rightarrow \pi^*$ transition. After irradiating the solution with UV (254 nm) in different periods 5, 10, 15, 25, 35, 45 min, the intensive peak at 256 nm decreased and two new strong absorption bands at 352 and 537 nm appeared with gradually increasing intensity. UV–VIS spectra indicated that after 45 min of irradiation, the open form was transformed to the closed-form (inset of Fig. 3a) and a photo-stationary state was reached. Upon irradiation with visible light (578 nm), the violet solution of closed-form was completely bleached, and the absorption spectrum returned to that of open form.

Despite the application of suitable UV light for an extended period,



Fig. 3. a) Time dependant UV–VIS spectra of H₂HA in methanol solution upon irradiating with 254 nm. The inset shows the ring-open and ring-closed form of the ligand. b) Solid-state UV–VIS spectra of H₂HA (red line for open form and black line for closed-form) and dehydrated compound \hat{I} before (green line) and after UV irradiation (orange line). The inset shows optical images corresponding to the colour changes of the crystals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the synthesized sample of *I* remained without any colour change, which was consistent with its C··C distance 4.148(6) Å of the active carbons. Surprisingly, the compound underwent a photochromic reaction after dehydration, which was confirmed by optical microscopy, UV/VIS measurements and also by DFT computations. Within TG measurements, a sample of *I* was heated initially to 200 °C, whereupon it transformed to the dehydrated form \hat{I} . The particles of \hat{I} turned to violet upon irradiating with 254 nm UV light, while they still retained their shape and the observed colour change was attributed to the formation of the closed-ring form isomer of the HA linker.

3.7. DFT calculations

The possibility of switching process occurring after dehydration was examined using DFT computations [9]. Fig. 4a-d show changes in interatomic separation between the active carbon atoms by releasing gradually water from the monomeric unit. In the case of the as-synthesized complex, the C···C distance was 4.148 Å, which decreased to 3.880 Å after removing one water molecule, resulting from the formation of an intramolecular hydrogen bond between the carboxylate oxygen atoms and the coordinated water molecule. In the models of monohydrate and anhydrous complexes, the C···C separations were exceedingly large for possible photochemical reaction, with respective values 4.639 Å and 4.653 Å. Therefore, a dimeric unit was chosen for DFT modelling, which was closer in its composition to the polymeric crystal structure of *I*. As evident from Fig. 4e, this dimeric unit undergoes structural changes after dehydration, through which the C··C distance becomes reduced to 3.814 Å. This distance is sufficiently short to react by UV irradiation. The results of DFT modelling confirm the possibility of ligand switching in the solid phase, which was also confirmed by optical microscopy (see Fig. 3b and Fig. S8 in ESI) and UV/VIS measurements (see Fig. 3b above).

4. Conclusion

In conclusion, the compound with composition $\{[Zn(\mu_3-HA)]$ $(H_2O)_3$]· H_2O _n was synthesized and structurally characterized. The chemical composition of the as-synthesized form was analysed by CHNS (elemental analysis) and FAAS (flammable atomic mass spectrometry) analysis, IR (infrared spectroscopy), TG (thermogravimetry), PXRD (powder X-ray diffraction) and SXRD (single-crystal X-ray diffraction). Based on SXRD, the solid-state arrangement of *I* is formed by a linear chain polymer composed of 1,2-bis(5-carboxylate-2-methylthien-3-yl) cyclopentene (HA), water molecules and Zn(II) ions. The switching properties of H₂HA ligand in methanol solution, the as-synthesized coordination polymer I and its dehydrated form \hat{I} in the solid-state were investigated by switching experiments driven by UV irradiation. The assynthesized form does not show switching after irradiation with UV light in solid-state, which is consistent with the diffraction results (C-C, d = 4.148(6) Å). Surprisingly, the compound undergoes a photochromic reaction after dehydration, confirmed by optical microscopy, solid-state UV/VIS measurements and DFT studies. We conclude that although structural features may sometimes prove to be unfavourable for switching conditions, this process can be achieved by post-synthetic modification of the sample, such as dehydration.

CRediT authorship contribution statement

Miroslav Almáši: Writing - original draft, Writing - review & editing, Synthesis, Characterization. Martin Walko: Synthesis, Characterization. Jana Boržíková: Synthesis, Characterization. Róbert Gyepes: Characterization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119879.



Fig. 4. Results of DFT modelling for a-d) step-by-step dehydration process of the monomeric unit and e) dehydrated dimeric unit with corresponding C--C distance between active carbon atoms.

References

- [1] J. Zhang, Q. Zou, H. Tian, Chem. Mater. 25 (2013) 378.
- [2] B.L. Feringa, Angew. Chem. Int. Ed. 56 (2017) 11060.
- [3] W.R. Browne, J.J.D. de Jong, T. Kudernac, M. Walko, L.N. Lucas, K. Uchida, J.H. van Esch, B.L. Feringa, Chem. Eur. J. 11 (2005) 6414.
- [4] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev. 114 (2014) 12174.
- [5] T. Fukaminato, S. Ishida, R. Métivier, NPG Asia Mater. 10 (2018) 859.
- [6] K. Matsuda, K. Takayama, M. Irie, Inorg. Chem. 43 (2004) 482.
- [7] J. Han, M. Maekawa, Y. Suenaga, H. Ebisu, A. Nabei, T. Kuroda-Sowa,
- M. Munakata, Inorg. Chem. 46 (2007) 3321.
- [8] K. Matsuda, Y. Shinkai, M. Irie, Inorg. Chem. 43 (2004) 3774.
- [9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R.

Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian 16 Revision A.03, Gaussian, Inc., Wallingford CT, 2010; M. Almáši, V. Zeleňák, R. Gyepes, S. Bourrelly, M.V. Opanasenko, P.L. Llewellyn, J. Čejka, Inorg. Chem., 57 (2018) 1774.

- [10] G.M. Sheldrick, A. Crystallogr, C. Sect, Struct. Chem. 71 (2015) 3.
- [11] K. Brandenburg, H. Putz, DIAMOND–Crystal and Molecular Structure Visualization, version 4.5, Crystal Impact GbR, Bonn, 2017.
- [12] L.N. Lucas, J.J.D. de Jong, J.H. van Esch, R.M. Kellogg, B.L. Feringa, Eur. J. Org. Chem. (2003) 155.
- [13] M. Akazawa, K. Uchida, J.J.D. de Jong, J. Areephong, M. Stuart, G. Caroli, W.R. Browne, B.L. Feringa, Org. Biomol. Chem. 6 (2008) 1544.
- [14] D.J. van Dijken, J.M. Beierle, M.C.A. Stuart, W. Szymański, W.R. Browne, B.L. Feringa, Angew. Chem. Int. Ed. 53 (2014) 5073.