

Supporting information

Exploring Multiple Functions of Diarylsemipinacol to Saturated Ethylene-Propylene Elastomer: From the Dynamic Covalent Networks to Tailoring its Macroscopic Performance

Youwei Ma,[†] Yufei Shen,[†] Zhiyong Liu,[†] Zixing Shi,^{*,†} Jie Yin,^{†,‡} and Ming Tian^{*,§} Rongjun Qu,[£]

[†]School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composite Materials and Shanghai Key Lab of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, 200240, China

[‡]School of Physical Science and Technology, Shanghai Tech University, Shanghai, 201210, China

[§]State Key Lab of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China

[£]School of Chemistry and Materials Science, Ludong University, Yantai 264025, China

1. Experimental Section

Materials. EPM (PetroChina Jilin Petrochemical J0010, 46-50 wt % ethylene, $M_n \sim 100000$ g/mol) was purchased from Jilin Petrochemical. Benzophenone (BP), Hexamethylene diisocyanate (HDI), N,N-dimethyl formamide (DMF), Dicumyl peroxide (DCP), Ethanol, Hexane, Toluene were received from Sinopharm Chemical (Beijing, China) without further purification. Chloroform (>99%, Aldrich Chemical, Shanghai, China) was refluxed and distilled for dehydration. 2-Amino-4-hydroxy-6-methylpyrimidine, dibutyltin dilaurate (DBTL) were obtained from J&K Scientific (Beijing, China).

Synthesis of EPM-6.5DASP. Firstly, 10g BP and 20g EPM were dissolved in toluene. Then, the mixture was exposed to 365 nm ultraviolet lamp for 12 h under N_2 atmosphere. After reaction, the mixture was precipitated in ethanol. The obtained product was dried on vacuum oven at 60 °C overnight. The graft ratio of DASP onto EPM identified by 1H NMR (Figure S1) was 6.5 mol%.

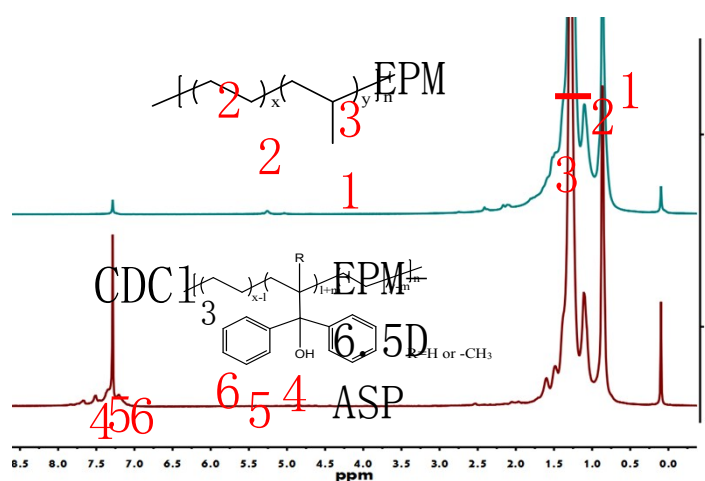


Figure S1 1H NMR spectra of EPM and EPM-6.5DASP in $CDCl_3$

Synthesis of 2-(6-isocyanato-hexylamino)-6-methyl-4[1H]-pyrimidone. The synthesis of 2-(6-isocyanato-hexylamino)-6-methyl-4[1H]-pyrimidone (UPy-NCO) was carried out according to a literature [1]. In detail, 2-Amino-4-hydroxy-6-methylpyrimidine was mixed with HDI at a molar ratio of 1 to 6. The mixture was put in a round bottom flask and stirred at 100 °C for 24 h under the condition of N_2

atmosphere. The reaction mixture was extensively washed by hexane to remove the unreacted hexamethylene diisocyanate. The product was dried at 50°C under vacuum overnight to further purify. The ^1H NMR of it was shown in Figure S2.

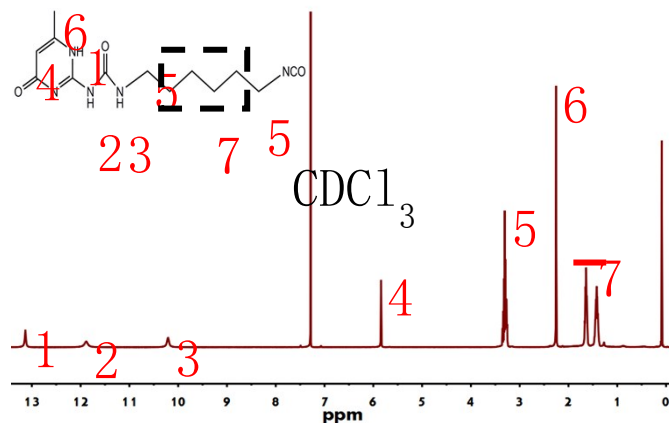


Figure S2. ^1H NMR spectra of UPy-NCO

Synthesis of EPM-xUPy. EPM-xUPy means EPM grafted with x mol% of UPy. The synthesis procedure of EPM-xUPy was described as follows. To a solution of 3 g EPM-6.5DASP in 100 mL chloroform, different weight of UPy-NCO (1 g, 2 g, 3.2 g, 4 g) was added each time. After addition of 2 drops of DBTL, the mixture was stirred at 60 °C for 16 h. Afterwards, the obtained solution was precipitated and washed with DMF several times, which was then dried at 60 °C under vacuum overnight. The relationship between the graft ratio and feed ratio of UPy-NCO to EPM-6.5DASP was displayed in Figure S3, which almost obeyed linear rules.

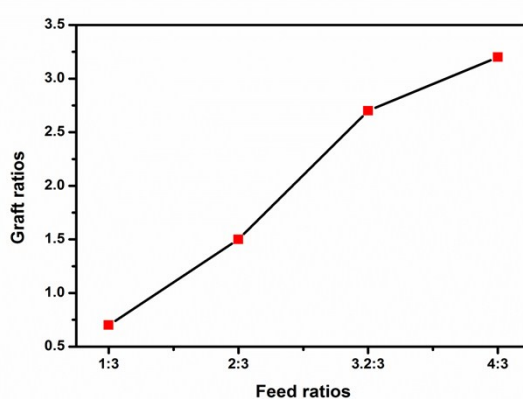


Figure S3 The relationship between feed ratio of Upy-NCO to EPM-6.5DASP and Graft ratio

Synthesis of EPM-xUPy-HDI networks. The content of HDI was controlled to be 2 mol% relative to the degrees of polymerization of EPM. They were dissolved in chloroform, and then treated with ultrasonic for 20 minutes. Next, the solution was poured into Teflon mold to evaporate chloroform at room temperature. Finally, the film was heat-treated at 80 °C for 24 hours to complete the crosslinking reaction.

Synthesis of EPM-DCP networks. 10g EPM and 0.125g DCP were dissolved in toluene. Then, the mixture evaporated completely at room temperature. The resulting polymer was vulcanized by compression molding for 30 min at 175 °C and 100 bar to obtain DCP crosslinked EPM (EPM-DCP) .

Swelling test of EPM-xUPy-HDI networks. The stripe samples (m_d) were immersed in the chloroform at 50 °C for 24 h firstly. Then the swollen sample was wiped by the filter paper and weighted quickly, each group of samples was measured three times to get its average swollen weight (m_s). The swelling ratio (Q) of EPM-xUPy-HDI is defined as: $Q = (m_s - m_d) / m_d$.

Shape memory and solid plasticity experiments. For the shape memory experiments, the stripes or films (permanent shape) were firstly configured into spiral shape or 3D frog shape respectively with applied stress at 90 °C, which were then cooled to 20 °C to fix these shapes. After the applied stress was removed, the temporary shapes were obtained. When reheated to 90 °C, they were expected to recover to their original shapes. For solid plasticity experiments, the film just recovered from 3D frog shape is permanently configured into frog shape through origami technique at 175 °C. Afterwards, this frog as permanent shape was conducted another round of shape memory experiment.

2. Characterizations

The tensile mechanical tests and the recycle tensile tests were all performed on INSTRON 5969 instrument (USA) at a speed of 120 mm min⁻¹ under room temperature. At least three dumbbell-shaped specimens were tested to obtain the stress–strain plots.

Differential scanning calorimetry (DSC) analyses were carried out using DSC Q200 (TA instruments) with a cooling and heating rate of 10 °C/min. Stress relaxation analysis (SRA) was carried out on a DMA Q800 (TA Instruments, USA). In the SRA

test, a rectangular sample was first isothermal at a specified temperature for 1 min. Then an instantaneous 5% strain was applied to the sample and the stress was recorded at the same time. All the quantitative shape memory and plasticity experiments were conducted with the same DMA machine under stress controlled and strain controlled conditions, respectively. Specifically, shape fixity (R_f) and recovery (R_r) ratios were calculated by the following equations:

$$R_f = \varepsilon_f / \varepsilon_m$$

$$R_r = (\varepsilon_m - \varepsilon_r) / \varepsilon_m$$

where ε_m represents the maximum strain under load, ε_r is the recovered strain and ε_f is the fixed strain after cooling and restriction removal.

Electron paramagnetic resonance (EPR) measurements were conducted on a EMXplus spectrometer (Bruker Corporation, Germany). Modulation frequency and amplitude were 100 kHz and 0.1 mT, respectively.

Fourier transform IR (FT-IR) spectra were performed on a Perkin-Elmer Spectrum100 FTIR spectrometer (U.K.) with a heating cell. EPM, EPM-6.5DASP and EPM-xUPy were dissolved in chloroform and coated a thin film onto a KBr plate. The data was collected after chloroform completely evaporated.

Nuclear magnetic resonance spectra (NMR) were carried out on a Varian MERCURYplus 400 spectrometer (400 MHz, Inc., USA). $CDCl_3$ was used as solvent and TMS was used as an internal standard.

Self-healing property was conducted on Polarizing Optical Microscope (Leica Microsystems GmbH, Germany) equipped with heating stage.

Remodeling of cross-linked EPM was carried out on the Hydraulic Presses (LP-S-50). The cross-linked EPM films were firstly tailored into debris, then piled up into a steel mould ($50 \times 50 \times 1 \text{ mm}^3$) and remodeled at $175 \text{ }^\circ\text{C}$ and 100 bar for 2 hours.

The AFM was operated in tapping mode by using silicon cantilevers with a force constant of 40 N m^{-1} .

3. Additional Experimental Data

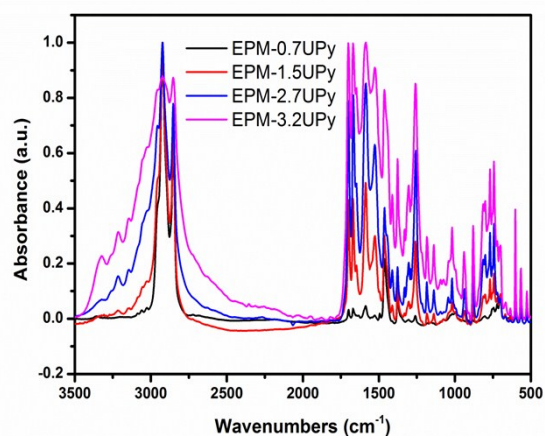


Figure S4 FTIR spectra of EPM-xUPy. The spectra are normalized by using the absorption intensity of -CH₃ at 2921 cm⁻¹ as an internal reference.

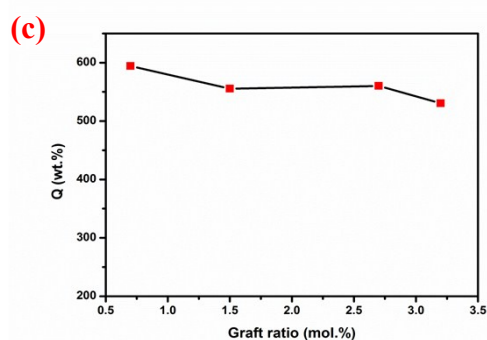
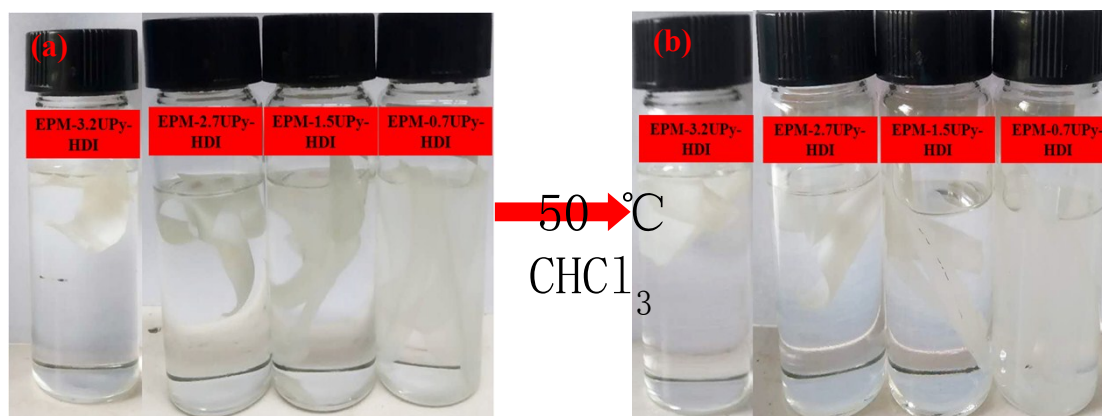


Figure S5. The images of EPM-xUPy-HDI before (a) and after (b) swelling in CHCl₃ at 50 °C for 24 h and swelling ratios (c).

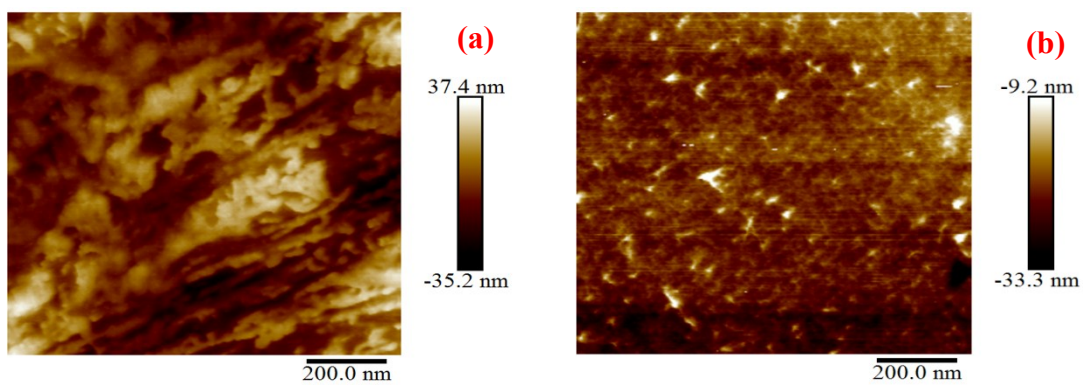


Figure S6. AFM height images of EPM-3.2UPy-HDI (a) and EPM-DCP (b).

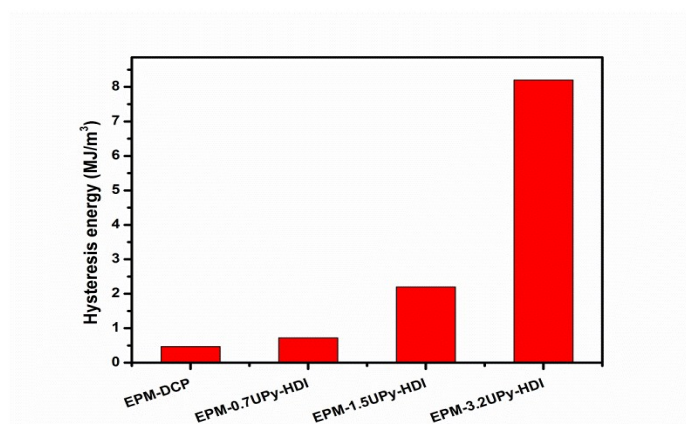


Figure S7. Hysteresis energy of EPM-DCP, and EPM-xUPy-HDI.

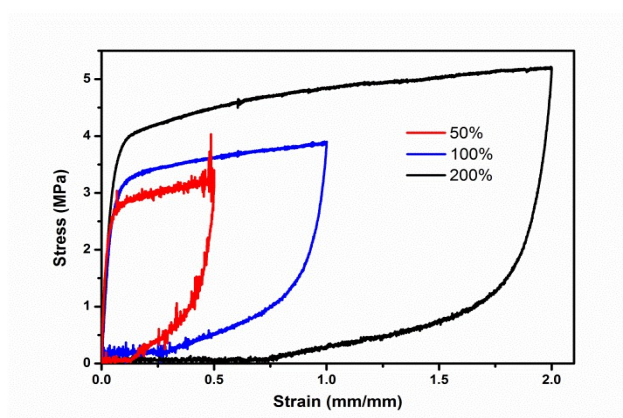


Figure S8. Loading-unloading cycles of EPM-3.2UPy-HDI at 50%, 100%, 200% strain

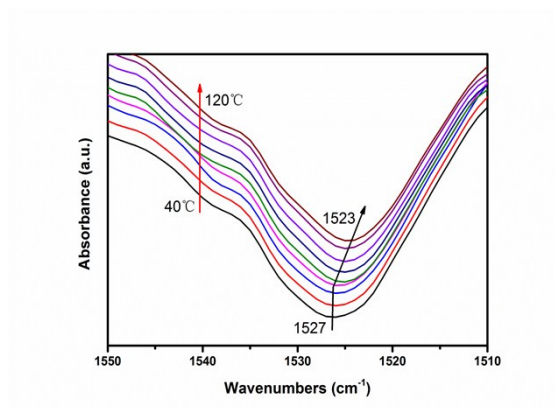


Figure S9. Variable temperature FTIR spectra for EPM-2.7UPy in the range of 1510-1550 cm⁻¹ from 40 to 120 °C with a temperature increment of 10 °C.

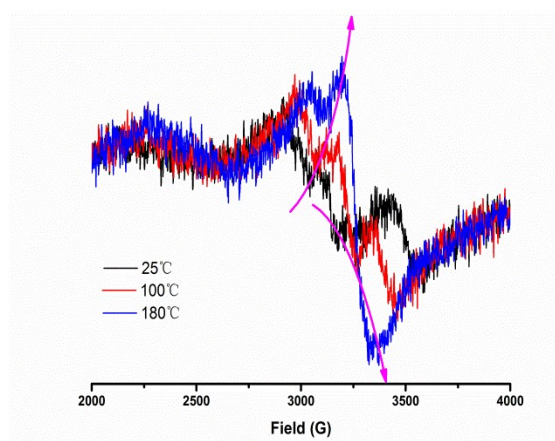


Figure S10. EPR spectra of EPM-2.7UPy-HDI at different temperature (25 °C, 100 °C, 180 °C).

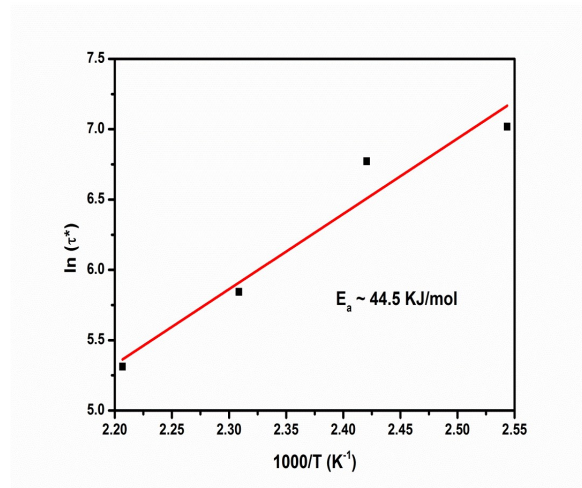


Figure S11. Fitting of τ^* to the Arrhenius equation for EPM-2.7UPy-HDI, τ^* is the relaxation time.

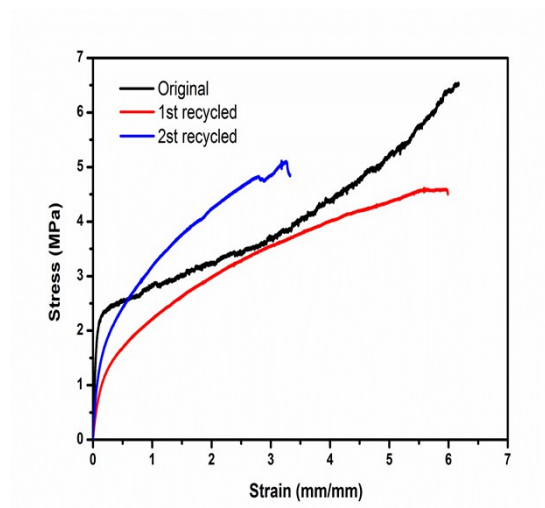


Figure S12. Stress-strain curves of EPM-2.7UPy-HDI after being remolding two times.

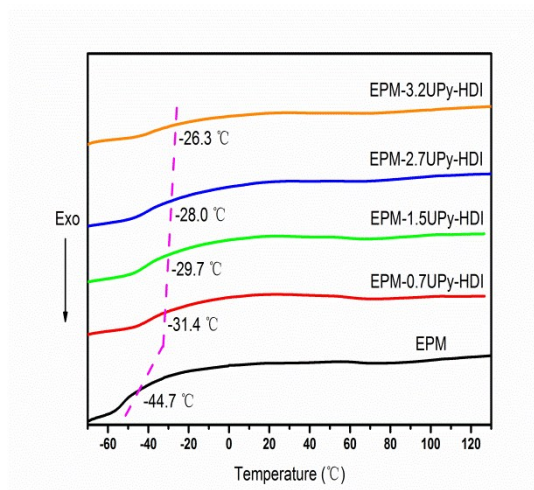


Figure S13. DSC curves of EPM and EPM-xUPy-HDI.

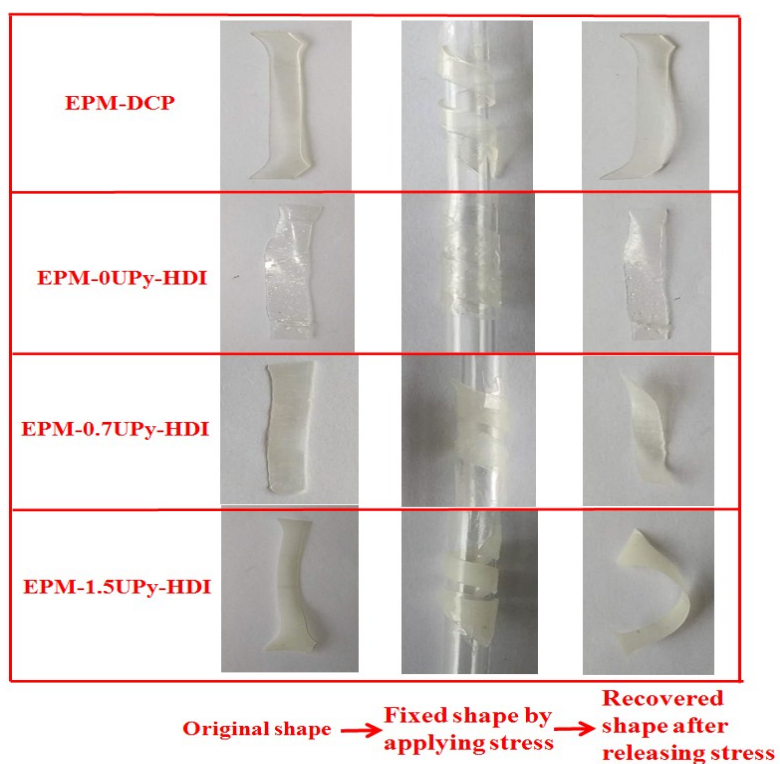


Figure S14. The images of EPM-DCP, EPM-0UPy-HDI, EPM-0.7UPy-HDI, EPM-1.5UPy-HDI, conducted by the same shape memory process to that of EPM-2.7UPy-HDI and EPM-3.2UPy-HDI .

Table S1. Comparison of mechanical properties of EPM-DCP and EPM-xUPy-HDI

	Tensile strength (MPa)	Strain at break (%)	Fracture energy (MJ/m ³)
EPM-DCP	1.4	440	3.6
EPM-0UPy-HDI	1.6	508	5.1
EPM-0.7UPy-HDI	2.8	663	10.3
EPM-1.5UPy-HDI	4.0	526	13.6
EPM-2.7UPy-HDI	6.5	617	24.5
EPM-3.2UPy-HDI	8.6	551	33.1

[1] Y. Song, Y. Liu, T. Qi, G.L. Li, Towards Dynamic but Supertough Healable Polymers through Biomimetic Hierarchical Hydrogen-Bonding Interactions, *Angewandte Chemie*, **57** (2018) 13838-13842.