Supporting Information

A Molecular Solar Thermal Energy Storage and Release System

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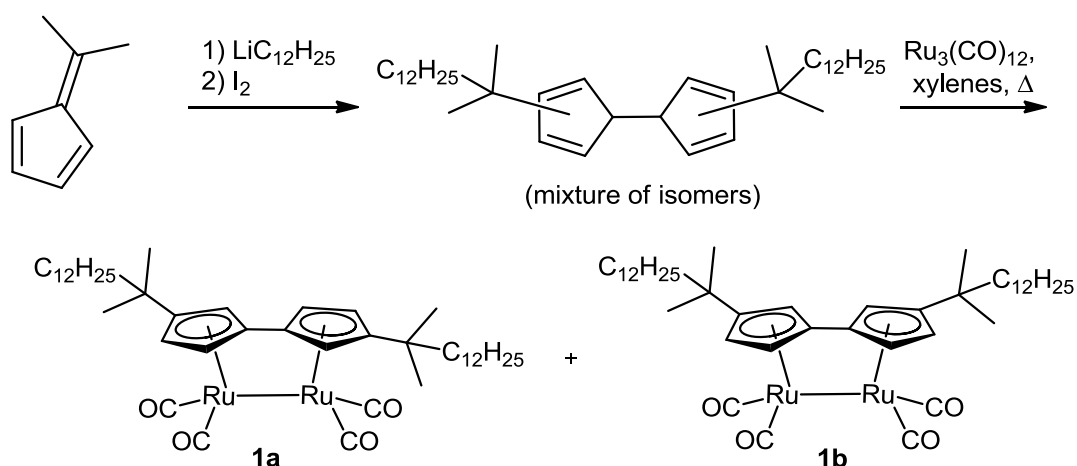[a] Chalmers University of Technology, Kemivägen 4, Gothenburg, 41296, Sweden
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1. Synthesis and Properties of Compounds 1 and 2

All reactions in the syntheses of compounds **1** and **2** were performed under Ar. Solvents were dried and degassed before use. All transfers occurred through rubber septa under Ar using cannula transfer or Ar-filled syringes. NMR spectra were recorded on Varian 400 MHz or Bruker 400, 500, or 600 MHz spectrometers. UV-vis spectra were measured on a Cary 50 instrument from Varian Inc. (Agilent Technologies). All starting materials were purchased from Strem or Aldrich Chemicals. Irradiation experiments are carried out with a 150 W Oriel solar simulator model 96000 equipped with an AM 1.5 filter (81094) and a 400 nm cut off filter from Newport Corp. A 150 W HQI lamp (Osram) was used for the stability tests.

Scheme S1

[3,3'-Bis(1,1-dimethyltridecyl)fulvalene]dirutheniumtetracarbonyl (1a and 1b). To 1-bromododecane (3.72 g, 15 mmol) in Et$_2$O (50 mL) at −78 °C was added dropwise *tert*-BuLi in pentane (18.25 mL, 1.7 M, 31 mmol). The mixture was stirred for 45 min at −78 °C,

warmed to 0 °C for 1 h, recooled to –78 °C, and then treated with a solution of 6,6–dimethylfulvene (1.49 g, 14 mmol) in THF (25 mL). The solution was allowed to warm to 0 °C for 1 h, then 20 °C for another h, and subsequently cooled to –78 °C, followed by the addition of a solution of I_2 (1.9 g, 7.5 mmol) in THF (15 mL). After warming to r.t. over 25 min, heptane (50 mL) was added and the mixture worked up with aq $Na_2S_2O_3$ (1 w%, 50 mL). The organic phase containing bis(1,1-dimethyltridecyl)dihydrofulvalene was dried over $MgSO_4$, placed in a round bottom flask equipped with a septum, and cooled to –78 °C. The cold solution was transferred by cannula to a boiling solution of $Ru_3(CO)_{12}$ (2.1 g, 3.3 mmol) in xylenes (80 mL) during 5 h. After additional heating to reflux for 12 h, the solvent was removed in vacuo. Column chromatography (CH_2Cl_2/pet ether, 1:5, on neutral Al_2O_3) afforded **1a** and **1b** (assumed to be 1:1) as a yellow oil [672 mg, 16% based on $Ru_3(CO)_{12}$], inseparable by further chromatography and giving rise to isochronous NMR spectra: ^{1}H NMR (400 MHz, C_6D_6) δ=5.11 (dd, J = 2.8, 1.8 Hz, 2 H), 3.63 (t, J = 1.8 Hz, 2 H), 3.10 (dd, J = 2.8, 2.0 Hz, 2 H), 1.43 (br t, J = 7.0 Hz, 4 H), 1.38–1.25 (40 H), 1.20 (s, 6 H), 1.02 (s, 6 H), 0.92 ppm (t, J = 6.9 Hz, 6 H); ^{13}C NMR (150 MHz, C_6D_6) δ=206.89, 206.45, 126.20, 92.05, 86.12, 76.50, 76.32, 45.57, 34.13, 32.67, 31.02, 30.50 (3 C), 30.46, 30.44, 30.16, 30.06, 29.24, 25.73, 23.46, 14.71 ppm; IR (film) $\tilde{v}$ =2957, 2921, 2852, 1996, 1954, 1913, 1467, 1398, 1385, 1364, 1059, 849 cm^{-1}; UV (toluene) λ_{max} (ε)=333 (7180), 390 nm (sh, 1550) (Fig. S1); MS (70 eV): m/z (rel intensity): 864 (M^+, 100), 806 (50), 741 (50), 371 (48). HRMS (ESI): calcd for $C_{44}H_{68}O_4Ru_2$: 864.3205; found 864.3227.
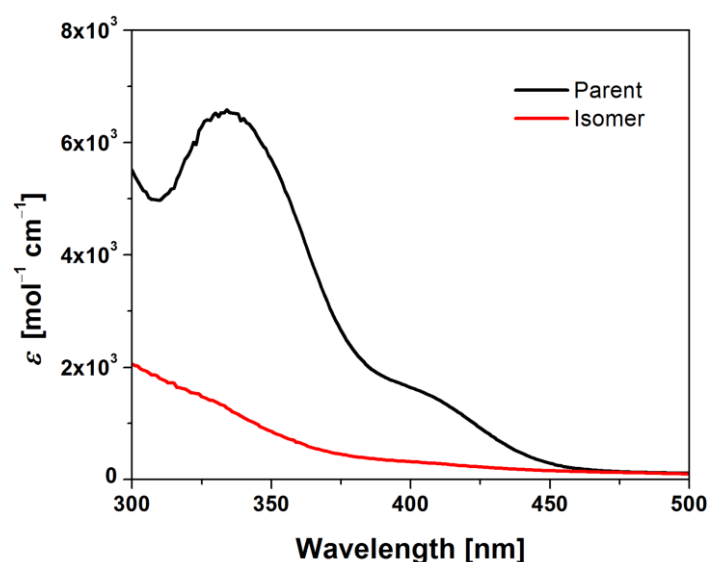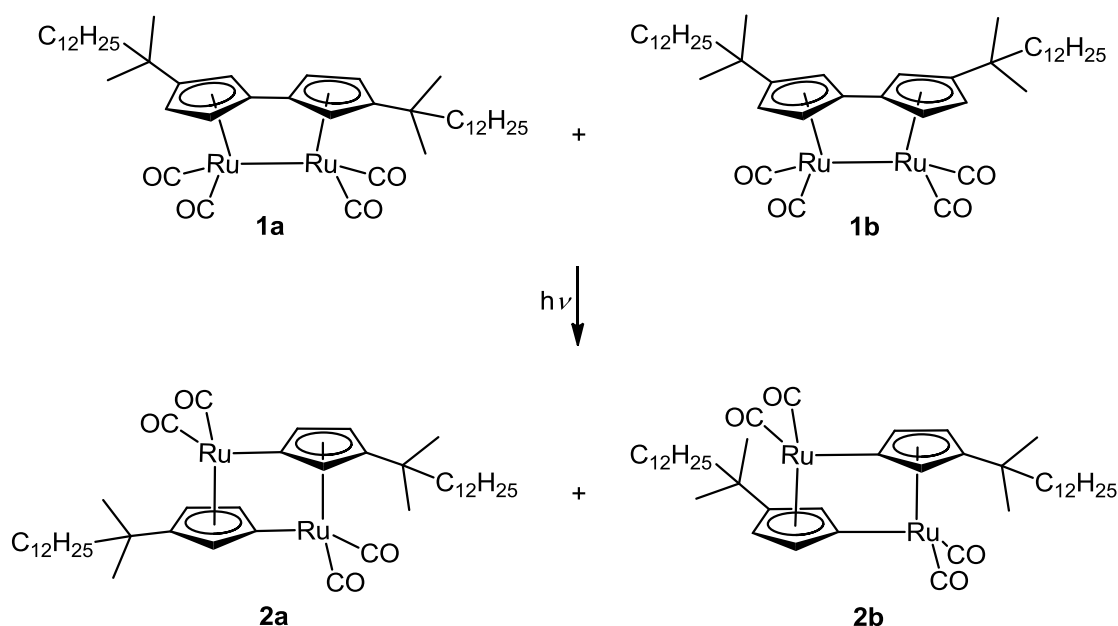

Fig. S1 Absorption spectra of **1a/1b** (parent) and **2a/2b** (isomer) in toluene.

Scheme S2

[μ_2-η^5:η^5-3-(1,1-Dimethyltridecyl)cyclopentadienyl]$_2$dirutheniumtetracarbonyl (2a and 2b). A mixture of **1a** and **1b** (1:1; 65 mg, 7.5 mmol) in dried and degassed toluene (30 mL) was placed in a sealed, thick-walled glass tube. The vessel was immersed in an aqueous solution of NaNO$_2$ (75 g in 100 mL) filter (cut off 400 nm) of 1.5 cm thickness. The temperature was maintained at 20 °C with a thermostated circulating bath and the sample irradiated with a 300 W GE-ELH projector or 150 W Osram HQI-R150W/NDL metal halide lamp for 10 h. Evaporation of the solvent afforded isomers **2a** and **2b** (assumed to be 1:1) quantitatively (by ^{1}H NMR) as a colorless oil: ^{1}H NMR (600 MHz, C$_6$D$_6$) δ=4.91 (dd, J = 2.2, 1.9 Hz, 2 H), 4.82 (dd, J = 1.8, 1.8 Hz, 2 H), 4.27 (dd, J = 2.1, 2.0 Hz, 2 H), 1.38–1.21 (m, 40 H), 1.16 (m 4 H), 1.03 (s, 6 H), 0.92 (t, J = 7.0 Hz, 6 H), 0.88 ppm (s, 6 H); ^{13}C NMR (101 MHz, C$_7$D$_8$) δ 203.13, 202.20, 130.35, 95.40, 94.09, 88.75, 85.52, 45.37, 33.85, 32.68, 30.90, 30.50, 30.46 (3 C), 30.31, 30.15, 29.83 (2 C), 25.55, 23.46, 14.70 ppm; IR (film) $\tilde{v}$ =2959, 2927, 2854, 2005, 1955, 1467, 1367, 1323, 1056, 1031, 869, 844 cm^{-1}; UV (toluene) λ_{max} (ε)= 340 (sh, 1100), 380 nm (sh, 240) (Fig. S1); MS (70 eV): m/z (rel intensity): 864 (M^+, 48), 806 (21), 741 (21), 57 (100). HRMS (ESI): calcd for C$_{44}$H$_{68}$O$_4$Ru$_2$: 864.3205; found 864.3227; found 864.3202.
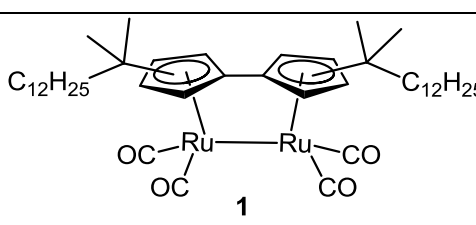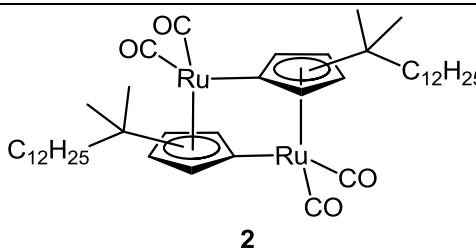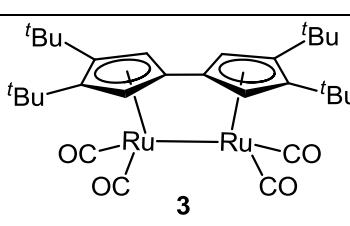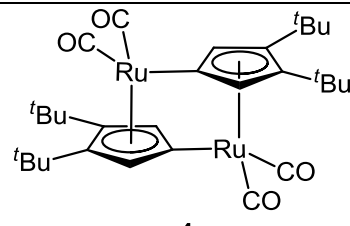
Isomerization of 2a/2b to 1a/1b. A solution of **2a/2b** (1:1; 5 mg) in THF-d_8 (0.5 mL) sealed in an NMR tube was heated at 90 °C for 1 h, after which starting material had reverted to **1a/1b** quantitatively, as monitored by ^{1}H NMR. A similar experiment was carried out at r.t.
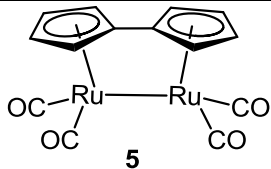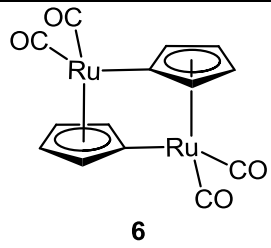
with added 1% AgNO$_3$ on silica (40 mg, 0.0023 mmol), leading to complete conversion in 15 min.

Durability of the photo-thermal cycle 1a/1b⇋2a/2b. To test the stability of the system in multiple cycles, **1** (5 mg) in toluene-d_8 was photoisomerised to **2** in a sealed NMR tube under Ar and subsequently regenerated at 90 °C for 3 h. Conversions were measured by ^{1}H NMR integration using the residual proton resonance in toluene-d_8. This sequence was performed 16 times and the results depicted in Fig. 4 of the main manuscript.

Solubility Measurements

Table S1 compares the solubilities of **1a/1b** and **2a/2b** with those of the tetra-t-butyl derivatives **3** and **4**, and the parent systems **5** and **6** in THF.

Compound	Solubility (mg/mL)
1	400
2	300
3	276
4	13

5	22
6	<1

Photoisomerisation Quantum Yield. The photoisomerisation quantum yield of **1** at 400 nm was determined in Ar-degassed toluene-d_8 solutions (2 mM). Irradiation was performed with a laser diode (400 nm, 10 mW) and the photoconversion to **2** measured by NMR spectroscopy. The optical density was kept above 2 to ensure complete absorption of photons by **1**.

Differential Scanning Calorimetry Measurements. Differential Scanning Calorimetry (DSC) measurements employed a TA Instruments Tzero Q20 differential scanning calorimeter. The oil of photoisomer **2** was subjected to high vacuum to remove residual solvent toluene (from its preparation) and a small, weighted amount placed on an aluminum DSC pan. The pan was hermetically sealed and placed into the DSC apparatus. The data were collected from –30 °C to 250 °C at a 10 °C/min heating rate. The exotherm observed during the heat release step **2→1** was integrated to obtain the energy/g stored in **2**. The flat portions of the DSC curve were used to obtain specific heat values of **1** and **2**. The averaged value for the $\Delta H_{storage}$ of **2** (5 measurements) was 110.8 J g^{-1}, that of the specific heat 1.23 J g^{-1} K^{-1} at 75 °C.

2. Device Fabrication

Solar collector. The solar collector was made of borosilicate glass anodically bonded at 400 °C and 800 V to a silicon substrate that contained etched microchannels. Openings for the inlet and outlet to the microchannels were predrilled. The microchannels were constructed on a 150 mm diameter silicon wafer (p-type, 1–10 ohm cm, [100]) by using photolithography with a Karl Suss MA6 Mask Aligner for defining their pattern. The latter was etched using a Surface Technology Systems (STS) DRIE etching tool. A ~50 μm depth was ascertained by using an Alpha-Step IQ Surface Profiler. The silicon substrate and borosilicate glass were thoroughly cleaned in piranha solution (H_2SO_4-H_2O_2, 4:1) and dried, before they were

bonded. The entire system was then placed on a 25 x 25 cm^2, 1 cm high aluminum heat sink. A CNC mill was used to machine two circular grooves to accommodate chemical resistant Viton O-rings on two separate aluminum plates (1 cm x 5 cm x 25 cm). Holes were then drilled concentric to the O-ring grooves. These openings were then aligned with those on the borosilicate glass and secured by clamp to create an air tight seal. A syringe tip was inserted and fastened by chemically resistant epoxy. Finally, PTFE tubes were used to connect the inlet of the microchannel to a WPI SP200i syringe pump containing compound **1** (0.1 M in toluene), and the corresponding outlet to an Ar-flushed container. The total surface area of the microchannels was 585 mm^2. Irradiation employed a full spectrum solar simulator lamp from Newport Corp., equipped with an AM 1.5 and <400 nm filters. Calibration to 1 sun intensity was made with a certified photovoltaic as a reference. The simulator was incorporated into the experimental setup as depicted in Fig. 2A of the main manuscript. A degassed solution of **1** was pumped through the apparatus and conversion to **2** monitored by ^{1}H NMR spectroscopy.

Heat release. Catalytic reactor experiments utilized a polytetrafluoroethylene (PTFE) tube inside a vacuum chamber ($p_{system} \approx 10^{-5}$ Torr, maintained via a Leybold Vacuum turbomolecular pump) designed to minimize convective and conductive heat losses and purchased from Kurt Lesker Inc. (Fig. S2). A channel T-junction allowed the introduction of thermocouples into the tube through one port, and the solution through the other. The former consisted of two SLE Omega Engineering thermocouples, placed just before and after the catalyst area and away from the chamber inlet and outlet. Cotton plugs prevented catalyst dislocation. The chamber temperature was monitored by two additional thermocouples inside the vacuum chamber, whereas the system pressure was recorded by a pressure gauge. Additional PTFE tubes connected the catalytic reactor to the syringe pump at the inlet and to the collection flask at the outlet, respectively. The time dependent temperature rise was measured at increments of 1 s with an Omega HH147U Data Logger Thermometer (0.1 °C resolution) and recorded directly on a computer. An experiment commenced by flushing the catalyst THF, followed by pumping the solution of **2** in THF through the system. The observed temperature rise is shown in Fig. 3 of the main manuscript.
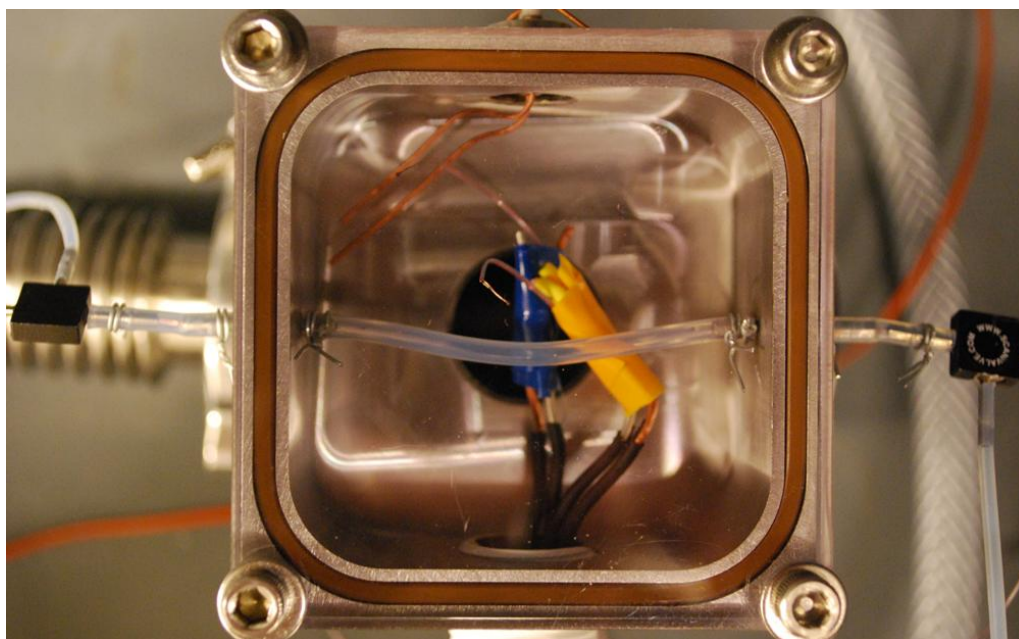
Fig. S2 Picture of of the catalytic reaction chamber.

3. Full cycle efficiency and potential improvements of MOST system

To estimate the round trip efficiency of the MOST system we considered the efficiency of conversion of **1**→**2** defined in eqn (S1),[1] and the efficiency of the thermally/catalytically triggered back reaction.

$$\eta = \frac{\Delta \hat{H}}{hcN_A / \lambda_{\text{lim}}} \cdot \frac{\int_{o}^{\lambda_{\text{lim}}} I_\lambda (\lambda / \lambda_{\text{lim}}) d\lambda}{\int_{0}^{\infty} I_\lambda d\lambda} \cdot \Phi \cdot \eta_{abs} 100 \qquad \text{(S1)}$$

Here η is the overall efficiency (%) of **1**→**2** conversion. The first term is the energy conversion factor which is the ratio of the molar enthalpy (stored energy in photoisomer **2**) to the energy of one mole of photons with the threshold energy λ_{lim} where c is the speed of light, h is Planck's constant, and N_A Avogadro's number. The second term is the fraction of energy useful for photoconversion of **1**→**2**; it is the ratio of useful energy (as determined by the absorption spectrum range of **1**) to the solar flux from the AM1.5 simulator used in the experiments. Because we implement a 400 nm cutoff filter in these experiments, the useful energy ranges from approximately 400–475 nm (also see Fig. S1). The useful energy ratio was determined from the specifications provided by the AM1.5 solar simulator vendor (Newport Corp.). The third term is the quantum yield Φ measured to be 0.02. Finally, the last

term is the overall absorption of **1** which can be estimated a $\eta_{abs}=1$ if long residence times are implemented and thus 100% conversion of **1** to **2** is achieved as observed experimentally.

Based on our experiments, the round trip efficiency of **1→2** considering eqn (S1) and nearly 98% conversion during the catalytic/thermal reversal reaction is approximately 0.071%. This efficiency does not include losses via heat exchange, a portion of the MOST system that can be optimized separately. By considering extensive work that has been performed on the N-Q system in the past several decades,[2–7] we estimate that the peak efficiency of the MOST system can be near 8.8%. In this assumption we estimate Φ~0.95 and the range of wavelengths over which **1** absorbs to be 280–550 nm.

When considering large scale applications, recyclability of **1** and **2** through thousands of cycles is important. However, we have not considered this optimization here, and note that studies of other MOST candidate systems have shown that several thousand cycles can be achieved with minor degradation.[7,8]

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