A device for solar energy storage and release based on a reversible chemical reaction is demonstrated. A highly soluble derivative of a (fulvalene)diruthenium ($FvRu_2$) system is synthesized, capable of storing solar energy (110 J g^{-1}) in the form of chemical bonds and then releasing it „on demand“, when excited thermally or catalytically. A microfluidic device is designed and constructed for both the photo-harvesting and the heat-utilization steps, allowing for the recycling of material.

Utilization of solar energy in either photovoltaic or solar thermal power generation is limited by the inherent challenge of intermittency and load leveling.[1–3] In these power generation systems, development of large scale electrical and thermal energy storage technologies that would mitigate these constraints has been challenging.[1–7] In conventional oil- and coal-based power generation, energy that has been stored over geological time scales in the form of chemical bonds is released by combustion „on demand”. A great deal of current effort is devoted to mimicking this process on a shorter time scale by the creation of solar fuels via the splitting of water to form H_2 and O_2, or similar schemes to produce alcohols and other fuels from CO_2.[1,8,9] In this context, a closed cycle that reversibly stores energy upon exposure to sunlight (a photochemical reaction), followed by a second, on demand reaction, that generates heat and regenerates the original reactant, is very attractive as a renewable storage media for solar energy (Fig. 1A).[9] A molecule (the „parent“) must be photoconverted to a stable higher energy isomer (the “photoisomer”). The latter then releases its energy as heat by reversing to the parent on thermal excitation. The implementation of this concept is challenging, since the parent must efficiently absorb a maximum of the solar spectrum to generate the photoisomer at high quantum yield. The photoisomer must be stable and relatively optically inactive. These reactions should be associated with reasonably positive enthalpies (or free energies) of the photoconversion step, but possess kinetic stability with respect to the thermal release step, ideally triggered only by a suitable catalyst. Finally, the cycle should be stable with respect to degradation.[9–16]

A number of organic compounds have been scrutinized in these respects, most notably the norbornadiene-quadricyclane system.[10–15] Organometallic (fulvalene)diruthenium compounds ($FvRu_2$) have shown promising solar energy conversion and storage properties due to their inherent stability and large energy storage enthalpies (~195 J g^{-1}).[17–19]

Here, we report the design and construction of a microfluidic molecular solar thermal (MOST) device that uses a new bis(1,1-dimethyltridecyl) substituted derivative of $FvRu_2$ to demonstrate the technical feasibility of this concept (Fig. 1B). In the forward reaction, **1** is photoisomerized to **2** (energy storage), and in the reverse, a catalyst facilitates the stored heat release, yielding a measurable temperature rise. While the chemical aspects of

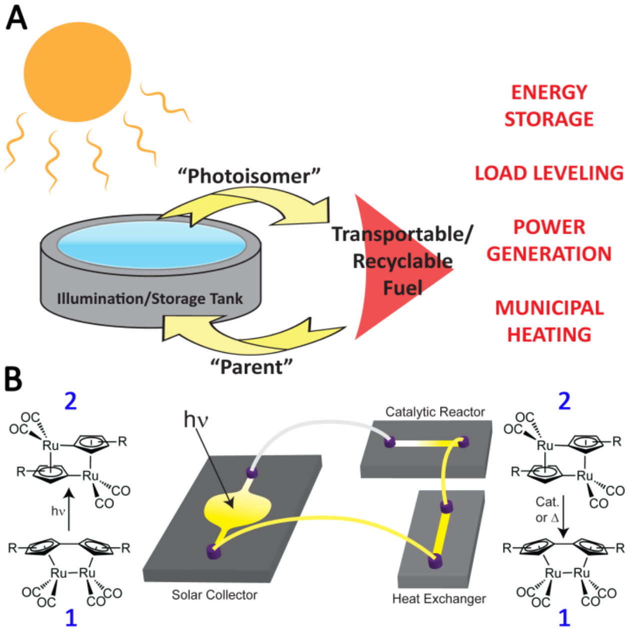

Fig. 1 (A) Conceptual illustration of a practical molecular solar thermal energy storage system, in which solar energy is harvested and used cyclically for „on demand" applications. (B) MOST device developed in this study: The working fluid contains compound **1** that is photoconverted in a high surface area solar collector to form **2** (R = 1,1-timethyltridecyl). The solution can be pumped directly into a heterogeneous catalytic converter, in which the stored energy can be extracted by heat exchange.

MOST suggest avenues for future optimization, the construct provides a proof-of-principle platform that should expedite the screening for improved molecular targets and catalysts.

The goal of this system is to maximize the temperature rise during the thermal isomerization step to allow for direct solar thermal applications via low temperature power generation systems.[20,21] An estimate of the expected temperature rise is given by eqn (1),

$$\Delta T_{\mathrm{adiabatic}} = \frac{m_{\mathrm{solu}}\,\Delta H}{(m_{\mathrm{solu}}\,C_{\mathrm{solu}} + m_{\mathrm{solv}}\,C_{\mathrm{solv}})} \qquad (1)$$

in which $\Delta T_{\mathrm{adiabatic}}$ is the total adiabatic temperature rise of the solution, ΔH the total energy stored per gram of isomer, m_{solu} is the mass of the solute (photoisomer), m_{solv} the mass of the solvent, C_{solu} the specific heat of the solute, and C_{solv} the specific heat of the solvent. As such, the presence of an inert solvent tends to dilute the temperature rise so the choice of **1** as the molecule with which to test a device was predicated by the need to attain high concentration.

The parent $\mathrm{FvRu_2(CO)_4}$[17] and its tetra-*tert*-butyl derivative[18] were unsatisfactory in this regard (see ESI†). Consequently, structure **1** was targeted, in which the long-chain tertiary alkyl group was hoped to improve solubility and also ensure regioselective assembly of the Fv core. In the event, **1** could be assembled in three steps, relying on existing methodology.[17,18,22]

Thus, 6,6-dimethylfulvene was treated with dodecyllithium to form (1,1-dimethyltridecyl)cyclopentadienyllithium, which was coupled *in situ* by I_2 to engender the corresponding dihydrofulvalene (mixture of stereoisomers). Subsequent metalation with $\mathrm{Ru_3(CO)_{12}}$ produced **1** as a yellow oil in 16% overall yield as a mixture of two diastereomers (see ESI†).

Upon irradiation with a high intensity halogen or, simply, a projector lamp (aq $\mathrm{NaNO_2}$ filter,[23] cut-off <400 nm, 10 h), **1** underwent photoinduced isomerization quantitatively to form colorless photoisomer **2**. The UV-vis spectra (see ESI†) quantify photobleaching, a desirable property for applications. This process was completely reversed on heating to 90 °C for 60 minutes (see ESI†). The robustness of the system was tested in a series of 16 complete conversion cycles in a sealed NMR tube, revealing excellent stability up to 10 iterations (Fig. 2).

The solubility of both isomers is about 0.4 M (≈350 mg $\mathrm{mL^{-1}}$) in common organic solvents, such as THF or toluene. Differential scanning calorimetry (DSC) measurements of the **2**→**1** conversion reveal that 110 J $\mathrm{g^{-1}}$ are stored in the chemical bonds of photoisomer **2**, a value comparable to that of the parent $\mathrm{FvRu_2(CO)_4}$ (see ESI†).[19] Entering these numbers into eqn (1), a maximum temperature rise of approximately 23 °C in THF can be expected.

A microfluidic reactor was constructed for the conversion of **1** to **2** under natural irradiation conditions (1 sun, AM 1.5). The MOST solar collector (Fig. 3A) consists of a micro-fluidic system in which the working fluid (**1** dissolved in toluene at 0.1 M concentration) is pumped through the device while being illuminated by a solar simulator. The irradiated microchannel area of 585 mm^2 was limited by the focus size of the solar simulator. By adjusting the flow rate from 4 μL min^{-1} to 0.1 μL min^{-1}, and thus the residence time in the reactor, conversions from 8 to 81% yield were achieved, respectively. It should be noted that these numbers are

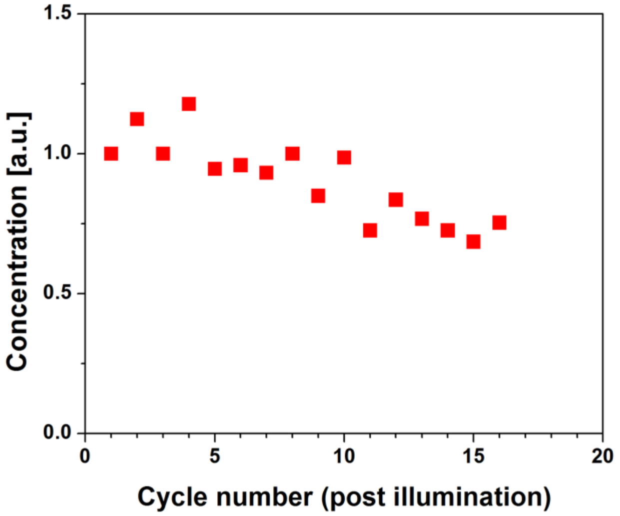

Fig. 2 Stability test of the **1**⇆**2** cycle demonstrated by monitoring the concentration (arbitrary units) of **2** after illumination in each cycle. Each full cycle iteration consists of a photochemical conversion followed by a heat induced back reaction, monitored by ^{1}H NMR (see ESY†).

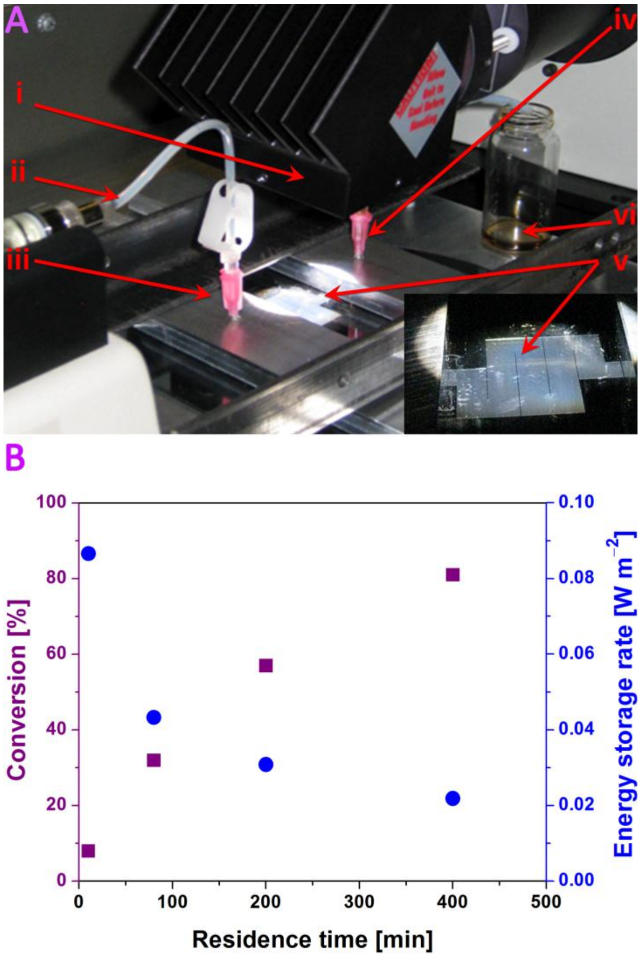

Fig. 3 (A) Solar thermal energy conversion device: (i) AM 1.5 solar simulator incorporating a 400 nm cut-off filter, (ii) syringe pump to adjust flow rate, (iii) inlet port of solution, (iv) outlet port of solution, (v) microfluidic plates, (vi) collector of irradiated solution. (B) Conversion of **1** (purple) to **2** (monitored by NMR) and energy storage characteristics (blue) as a function of residence time. Energy storage rate=[conversion rate (mol s^{-1}) x storage enthalpy (J mol^{-1})]/area of irradiation (W m^{-2}).

limited only by the residence time in the solar collector, as **1** transforms to **2** quantitatively in preparative experiments. By considering light out-put, residence time, concentration of **1**, and the conversion yield, the effective stored energy per unit area could be determined (Fig. 3B). As expected, the energy storage capacity declines with longer residence times, because **1** is depleted and therefore the amount of absorbed light quanta per unit time is lowered. In addition, prolonged exposure appears to cause some degradation, as evidenced by the formation of a thin film on the glass plate, which, apart from draining some material, may block penetration of the incident light. An independent order-of-magnitude measure of the energy absorbing capacity of **1** could be obtained from the quantum yield of the photoisomerization at 400 nm, Φ=0.002,[23] recorded with a continuous wave laser diode (see ESI†) and translating to a solar energy storage of 0.05 W m^{-2}.

For the second complementary part of the system, we needed to demonstrate that the energy stored in the active compound **2** can be effectively released by a triggered chemical back reaction. We have screened a number of potential catalyst systems and found that 1–10 w% $AgNO_3$ on silica catalyzes the reaction of **2** to **1** dissolved in THF in quantitative yield in less than 1 min. A limit of this catalytic system is the turnover number (TON) of only about 30, caused by catalyst (but not substrate) decomposition.[24]

To quantify the experimental temperature rise, we have developed a reactor chamber with the schematic shown in the insert of Fig. 4 (see also ESI†). Here, a THF solution of compound **2** is pumped through a

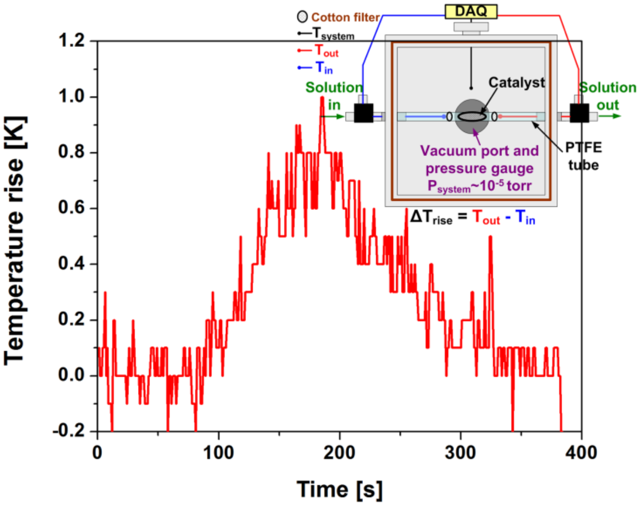

Fig. 4 Schematic of the catalytic reaction chamber used to measure the temperature rise via a data acquisition unit (DAQ) as a function of time, for **2** dissolved in THF (0.14 M), at a flow rate of 10 ml h^{-1}, through the catalyst (28 mg of 10 w% $AgNO_3$ on silica powder).

PTFE tube containing the catalyst (10 w% $AgNO_3$ on silica). The reactor tube is located inside a low pressure chamber ($P_{system}\approx10^{-5}$ torr), in order to minimize conductive and convective heat losses to the surroundings. Thermocouples are placed inside the reactor tube immediately before and after the catalytic material to minimize heat loss due to thermal conduction within the solution. Fig. 4 depicts the measured temperature rise ΔT_{rise}. This demonstrates that flow through a heterogeneous catalyst is a feasible way of extracting the stored energy in a MOST system (see also ESI†). The low TON of the catalyst limits the maximum observed temperature rise to approximately 0.9 °C, well below the theoretically predicted value from eqn (1). Clean catalytic conversion of **2** to **1** as indicated by NMR measurements demonstrates that the catalytic conversion in high yield is feasible (up to 98%), and that even better heat release characteristics can be expected if a more stable catalyst is implemented.

Putting into perspective the characteristics of the MOST system probedd here, we point out that its energy density at peak solubility is ~10.7 Wh/L. This is an orders of magnitude improvement to the original FvRu compounds,[17] and going in the right direction toward energy densities achieved in Li-ion batteries,[25] and those in recently proposed azobenzene systems.[26] For large scale applications, the mismatch between the rates of solar energy storage **1**→**2** and catalytic heat release **2**→**1** can be mitigated by proper MOST system design; **1**→**2** can be done in large storage tanks taking advantage of quantitative volumetric conversion in solution. Other important metrics of MOST systems to consider are the round trip efficiency and the number of cycles sustained before significan degradation occurs. Considering the former, with high catalytic conversion yield observed experimentally (~98%) and minor degradation, the full cycle efficiency of **1**⇆**2** (excluding losses via heat exchange) is ~0.071% (see ESI†). In view of the modifications implemented in systems such as norbornadiene-quadricyclane,[10–15] the efficiency of **1**→**2,** and thus the round trip efficiency, can analogously be improved by use of sensitizers, and additional substituents that would modify the absorption spectrum and quantum yield of the reaction. Under these premises, we estimate peak round trip efficiencies of **1**⇆**2** of up to 8.8% (see ESI†) which is comparable to the estimated peak efficiencies of photosynthesis-biomass processes.[27] Although not established in this study, studies of other MOST candidate systems have shown that several thousand cycles can be achieved with minor degradation.[15,28] Given the experimentally observed stability of the MOST implemented here, nothing suggests that this cannot be achieved with further MOST system optimization.

In summary, we have demonstrated a full cycle MOST energy storage and release system. It consists of a $FvRu_2$ working fluid, a microfluidic solar collector, and a catalytic heat release reactor. The high solubility of the newly synthesized **1** provides a large energy storage density in the working fluid and the catalytic energy release reaction is rapid, two important factors for device implementation. The kinetic stability of **2** and the resilience of the **1**⇆**2** cycle are promising characteristics that encourage further improvements of the framework. Temperature rise is currently limited by catalyst performance, suggesting that in addition to optimization of the parent molecule for light absorption features, further catalyst development is necessary. Moreover, from an economical perspective, ruthenium based compounds are not ideal due to scarcity and high cost of this metal, thus development of photosensitive organometallic compounds based on abundant metals such as iron is highly desirable. The availability of a MOST device will facilitate the screening for alternative molecular systems and catalysts, in an effort develop an economically sound system.

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† Electronic Supplementary Information (ESI) available: Additional information regarding chemical synthesis and characterization, quantum yield experiments, solubilities, differential scanning calorimetry measurements, device fabrication, and temperature rise determinations. See DOI: 10.1039/b000000x/

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