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Reversible Photocuring of Liquid Hexa-Anthracene Compounds for Adhesive Applications

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ABSTRACT

Reworkable adhesion of glass plates was demonstrated using colourless adhesives. This was achieved using anthracene-terminated liquid compounds with hexamer structures (2500 g mol^{-1}) as adhesives, which are photo-crosslinkable and thermo-degradable materials. It was found that the substitution position at the anthracene was important to obtain liquid-phase compounds at room temperature. However, although the compounds were liquid, they were too viscous to be used as adhesive. Therefore, they were mixed with 25 wt.% of dibutyl phthalate to increase fluidity. The liquid mixture could then be applied to the glass substrates without further modification, and was curable via photodimerisation of anthracene moieties to tightly attach the glass substrates together. The cured material was stable up to 120°C , but it returned to the original liquid state at room temperature after heating at 180°C , resulting in the detachment of the substrates without applying any strong force. The cycles of the curing and liquefying processes was reproducible for at least five consecutive times.

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Introduction

Adhesive bonding is widely used for product manufacturing. The debonding function of adhesive joints is recently attracting attention to promote the recycling of various product parts and repairing of the product. Debonding systems such as utilisation of thermally expandable particle and degradative reaction have been proposed previously. ^[1–3] They are basically irreversible systems. Regeneration of the liquid and cured states of adhesives at room temperature is required to facilitate the repair process. The principle of repeatable adhesion is based on the reversible change of the melting or softening point of the adhesive, which is associated with the reversible photoreaction. Thus, liquid and solid states of the compound can appear alternatively at room temperature, depending on the chemical structures of the photoreactive compound before and after the

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photoreaction. Consequently, the adhered glass substrates cannot be separated when the adhesive is solid, while they can be easily separated without any applied force when the adhesive becomes liquid. Reversible adhesion of glass plates has been recently demonstrated using a material that can switch between solid and fluidic states when irradiated alternatively with visible and ultraviolet light. [4–8] The adhesive materials used had 4–8 hexylazobenzene-oxyundecanoyl groups connected by a sugar alcohol scaffold or alkylazobenzene side chains of a polyacrylate main chain. The azobenzene moieties are trans-cis photoisomerisable and coloured units. In this case, the glass transition temperature of one hexamer among the adhesive materials is 80 °C in one state (trans-state of the azobenzenes), while it is lower than 10°C in another state (cis-state), allowing for this transition from liquid to solid and back to liquid depending on the light used for irradiation. However, due to the use of azobenzenes unit, the adhesives are coloured yellow or orange, which limits their application range.

This study aims at changing the photosensitive units from azobenzene to anthracene, which is transparent in the visible region, in order to achieve colourless adhesives. Anthracene is known for the photodimerisation and thermal cleavage characteristics of the obtained photodimer. [9–11] The reversible reaction of anthracene has already been applied to reversible phase transition [12–14] and healing polymers. [15] Moreover, if polyfunctional compounds with three or more anthracene units were synthesised, they could be photo-crosslinkable and thermo-degradable materials [16,17], which could function as reworkable adhesives. However, to be able to use them in a coating or deposition process on the surface of the adherend in the neat state, they should be liquid at ambient temperature. Thus, our target is to design and synthesise monomeric polyvalent anthracene derivatives that remain in a liquid state at ambient temperature. There are a few articles reporting a liquid derivative with polyfunctional anthracene. [17,18] They report that, if a molecule has a large number of anthracene units, it favors fast photocuring and guarantees the formation of three-dimensional photo-crosslinked structures, even under imperfect photodimerisation. However, the introduction of many anthracene units in molecular compounds increases their molecular weight and, in general, decreases their fluidity. In this study, in order to overcome this trade-off, polyvalent anthracene molecules in a liquid state at room temperature were successfully prepared. Furthermore, reversible adhesion of glass plates using the developed adhesives was demonstrated.

Experimental Procedures

Materials

Special grade potassium carbonate and 1st grade chloroform, dichloromethane, and hexane, and superhydrated N,N-dimethylformamide (DMF) and dichloromethane were purchased from Wako Pure Chemical Industry Ltd (Osaka,

Japan). N,N-dimethylamino pyridine, p-toluenesulfonic acid, N,N'-diisopropylcarbodiimide, 11-bromoundecanoic acid, D-sorbitol, anthracene-9-carboxylic acid, anthracene-1-carboxylic acid, anthracene-2-carboxylic acid and dibutyl phthalate were purchased from Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). The compounds were used as provided. N,N-dimethylamino pyridinium p-toluenesulfonate was synthesised from N,N-dimethylamino pyridine and toluenesulfonic acid as described in literature.^[19]

Analytical data for each synthetic compound was listed after the description of the corresponding synthesis method.

Step1: synthesis of 1,2,3,4,5,6-hexa-o-(11-bromoundecanoyl)-d-sorbitol

N,N'-Diisopropylcarbodiimide (1.00 g) was added under nitrogen atmosphere to 20 mL of dry dichloromethane solution containing 11-bromoundecanoic acid (2.00 g), D-sorbitol (0.18 g) and N,N-dimethylamino pyridinium p-toluenesulfonate (2.44 g). The mixture was stirred for 19 h. The resulting concentrated crude compound was purified by column chromatography using a mixture of dichloromethane and hexane (3:2) as eluent. A mass of 1.29 g of white powder was obtained (80.5%). Mp = 52.8–55.8°C, ¹H NMR (CDCl₃, δ): 1.28 (s, 60H, CH₂CH₂CH₂), 1.42 (q, J = 7.0 Hz 12H, CH₂C₂H₄Br), 1.60 (quin, J = 7.2 Hz, 12H, CH₂CH₂COO), 1.85 (quin, J = 7.1 Hz, 12H, CH₂CH₂Br), 2.24–2.39 (m, 12H, CH₂COO), 3.40 (t, J = 6.8 Hz, 12H, CH₂Br), 4.03 (dd, J = 11.9 Hz, 5.9Hz, 1H, H-1a), 4.06 (dd, J = 12.3 Hz, 5.4 Hz, 1H, H-6a), 4.25 (dd, J = 12.3 Hz, 3.5 Hz, 1H, H-1b), 4.36 (dd, J = 12.2 Hz, 3.7 Hz, 1H, H-6b), 5.02–5.08 (m, 1H, H-2), 5.19–5.24 (m, 1H, H-5), 5.39–5.46 (m, 2H, H-3, H-4). MALDI-TOF-MS: 1687.8 [M+Na]⁺, 1703.8[M + K]⁺.

Step 2a: synthesis of 1,2,3,4,5,6-hexa-o-[(anthracene-9-carboxyl)-11-undecanoyl]-d-sorbitol (9at6)

The 0.65 g of bromoundecanoate hexamer, 1.00 g of anthracene-9-carboxylic acid and 0.62 g of potassium carbonate were dissolved in 10 mL of dry DMF under nitrogen atmosphere. The mixture was stirred at 80 °C for 19 h under nitrogen atmosphere. The resulting concentrated crude compound was purified by column chromatography using chloroform as an eluent. A transparent liquid was obtained (0.88 g, 88.7%). ¹H NMR (CDCl₃, δ): 1.21–1.36 (m, 60H, CH₂CH₂CH₂), 1.43 (quin, J = 7.6 Hz 12H, CH₂C₂H₄OCO), 1.50–1.62 (m, 12H, CH₂CH₂COO), 1.81 (quin, J = 7.0 Hz, 12H, CH₂CH₂OCO), 2.22–2.37 (m, 12H, CH₂COO), 4.02 (dd, J = 12.1 Hz, 6.0 Hz, 1H, H-1a), 4.06 (dd, J = 12.2 Hz, 5.6 Hz, 1H, H-6a), 4.25 (dd, J = 12.2 Hz, 3.3 Hz, 1H, H-1b), 4.36 (dd, J = 11.9 Hz, 3.6 Hz, 1H, H-6b), 4.53–4.59 (m, 24H, CH₂OCO), 5.02–5.08 (m, 1H, H-2), 5.19–5.25 (m, 1H, H-5), 5.38–5.46 (m, 2H, H-3, H-4), 7.42–7.53 (m, 24H, ArH), 7.98 (d, J = 8.3 Hz, 12H, ArH), 8.01 (d, J = 8.2 Hz, 12H, ArH), 8.48 (s, 6H, ArH). MALDI-TOF-MS: 2512.6 [M] cation

radical, 2535.6 [M + Na]⁺, 2551.6 [M + K]⁺. Elemental analysis: Found: C, 75.20; H, 6.91. Calcd. for C₁₆₂H₁₈₂O₂₄: C, 77.42; H, 7.30.

Step 2b: Synthesis of 1,2,3,4,5,6-hexa-O-[(anthracene-1-carboxyl)-11-undecanoyl]-D-sorbitol (1At6)

The 0.65 g of bromoundecanoate hexamer, 1.00 g of anthracene-1-carboxylic acid and 0.62 g of potassium carbonate were dissolved in 10 mL of dry DMF under nitrogen atmosphere. The mixture was stirred at 80 °C for 12 h under nitrogen atmosphere. The resulting concentrated crude compound was purified by column chromatography using chloroform as an eluent. A transparent liquid was obtained (0.95 g, 95.7%). ¹H NMR (CDCl₃, δ): 1.23–1.40 (m, 60H, CH₂CH₂CH₂), 1.48 (quin, J = 7.2 Hz, 12H, CH₂C₂H₄OCO), 1.53–1.64 (m, 12H, CH₂CH₂COO), 1.82 (quin, J = 6.9 Hz, 12H, CH₂CH₂OCO), 2.24–2.38 (m, 12H, CH₂COO), 4.03 (dd, J = 12.8 Hz, 5.6 Hz, 1H, H-1a), 4.06 (dd, J = 12.8 Hz, 5.7 Hz, 1H, H-6a), 4.26 (dd, J = 12.2 Hz, 3.4 Hz, 1H, H-1b), 4.37 (dd, J = 12.1 Hz, 3.5 Hz, 1H, H-6b), 4.39–4.45 (m, 24H, CH₂OCO), 5.03–5.08 (m, 1H, H-2), 5.20–5.25 (m, 1H, H-5), 5.39–5.46 (m, 2H, H-3, H-4), 7.40–7.50 (m, 18H, ArH), 7.93–7.98 (m, 6H, ArH), 8.02–8.07 (m, 6H, ArH), 8.13 (dd, J = 8.4, 3.2 Hz, 6H, ArH), 8.19 (bd, J = 7.0 Hz, 6H, ArH), 8.40 (bs, 6H, ArH), 9.55 (s, 6H, ArH). MALDI-TOF-MS: 2512.5[M]cation radical, 2535.6 [M + Na]⁺, 2551.5 [M + K]⁺. Elemental analysis: Found: C, 76.29; H, 7.45. Calcd. for C₁₆₂H₁₈₂O₂₄: C, 77.42; H, 7.30.

Step 2c: synthesis of 1,2,3,4,5,6-hexa-o-[(anthracene-2-carboxyl)-11-undecanoyl]-d-sorbitol (2at6)

The 0.56 g of bromoundecanoate hexamer, 1.20 g of anthracene-2-carboxylic acid and 0.75 g of potassium carbonate were dissolved in 20 mL of dry DMF under nitrogen atmosphere. The mixture was stirred at 80 °C for 12 h under nitrogen atmosphere. The resulting concentrated crude compound was purified by column chromatography using chloroform as an eluent. A pale yellow solid was obtained (0.46 g, 53.8%). Crystal 1: 62.4: crystal 2: 83.0: isotropic liquid. The extinction coefficient of 9At6 at λ_{max} = 362 nm is 5.15 × 10⁴, which is six times higher than the reported value for methyl 9-anthracene carboxylate, 7800 L·mol⁻¹cm⁻¹[19] ¹H NMR (CDCl₃, δ): 1.25–1.40 (m, 60H, CH₂CH₂CH₂), 1.40–1.50 (m, 12H, CH₂C₂H₄OCO), 1.54–1.66 (m, 12H, CH₂CH₂COO), 1.79 (quin, J = 7.0 Hz, 12H, CH₂CH₂OCO), 2.22–2.40 (m, 12H, CH₂COO), 4.04 (dd, J = 12.1 Hz, 5.6 Hz, 1H, H-1a), 4.07 (dd, J = 12.5 Hz, 5.7 Hz, 1H, H-6a), 4.27 (dd, J = 12.2 Hz, 3.0 Hz, 1H, H-1b), 4.32–4.40 (m, 13H, H-6b, CH₂OCO), 5.07 (dd, J = 9.8 Hz, 5.6 Hz, 1H, H-2), 5.24 (dd, J = 9.9 Hz, 5.9 Hz, 1H, H-5), 5.39–5.47 (m, 2H, H-3, H-4), 7.42–7.51 (m, 12H, ArH), 7.92–8.20 (m, 24H, ArH), 8.36 (bs, 6H, ArH), 8.50 (bs, 6H, ArH), 8.74 (bs, 6H, ArH). Elemental analysis: Found: C, 76.67; H, 7.24. Calcd. for C₁₆₂H₁₈₂O₂₄: C, 77.42; H, 7.30, MALDI-TOF-MS: 2512.5 [M]cation radical, 2535.5 [M + Na]⁺, 2551.5 [M + K]⁺.

Physical Measurements

Several tests were conducted to determine the material compositions. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was conducted using a Bruker Daltonics autoflex speed-*AI* TOF/TOF instrument (Bruker Daltonics Japan; Yokohama, Japan) operated in the reflector mode. The samples were first prepared by mixing the toluene and ethanol (9:1) solutions of the compounds with α -cyano-4-hydroxycinnamic acid. Then, the solution was deposited on sample plates to be dried over air-blow.

The ^1H NMR spectra of the samples dissolved in CDCl_3 were recorded using a JEOL JNM-ECX-400 spectrometer (Tokyo, Japan).

Differential scanning calorimetry (DSC) was conducted at a heating and cooling rate of $10^\circ\text{C min}^{-1}$ by a Hitachi High-tech EXTAR6000 DSC instrument (Tokyo, Japan), where the sample of 5–10 mg was placed in sealing type aluminum pan (Hitachi High-tech P/N560-002) for measurement. The dynamic viscoelastic properties were measured by an Anton Paar MCR302 (Anton Paar Japan, Tokyo, Japan), where the sample thickness, the diameter and the frequency are $100\mu\text{m}$, 8 mm and 1 Hz, respectively. To analyse the thermal properties, the storage elastic modulus and loss elastic modulus were estimated for the samples cooled at 5°C min^{-1} from 150 to -10°C with the stress controlled at 10% from 150 to 70°C , 10 to 0.1% for 70 to 10°C and 0.1% for 10 to -10°C .

The absorption spectra were measured on a Agilent 8453 UV-Vis spectrophotometer (Agilent Technologies Japan, Ltd; Tokyo, Japan) in order to determine the colour and light absorption of the sample compounds. The solution samples were prepared by dissolving of 9At6 in ethyl acetate (Wako HPLC grade) (Osaka, Japan) at a concentration of $10^{-5}\text{ mol L}^{-1}$. The thin layer samples were prepared by placing the bulk materials in between two cover glass plates (\varnothing 15 mm), where the thickness was controlled by doping the materials with polymer beads with a diameter of 300 nm. The samples were irradiated to change the adhesive state from liquid to solid using high power light emitting diodes [CCS Ltd HLV-24UV405 for UV light ($\lambda = 405\text{ nm}$) (Kyoto, Japan)]. The light intensity was controlled to be 2 mW cm^{-2} .

The shear tension strength of the compounds on quartz plates was estimated by a single lap shear test, where two quartz plates ($10\text{ mm} \times 30\text{ mm}$, $t = 1\text{ mm}$), adhered to each other using the sample compounds, were pulled using a SIMADZU EZ-L tensile machine (Kyoto, Japan). Each quartz plate was connected to a thin stainless steel sheet ($10\text{ mm} \times 50\text{ mm}$, $t = 0.2\text{ mm}$) that was attached to an aluminum plate ($10\text{ mm} \times 30\text{ mm}$, $t = 1\text{ mm}$) to hold the sample. Each metal plate was attached with epoxy adhesives with an area of $10 \times 5\text{ mm}^2$ on the surface between quartz and steel and with an area of $10 \times 10\text{ mm}^2$ on the surface between aluminum and steel. The sample compounds were placed

between the two glass plates at 25°C. They were filled in an overlapped area of 1.0 cm × 0.5 cm, where the gap of the bondline was controlled to be 50 µm by doping with Cica Silica Gel 60N silica beads (Tokyo, Japan). The sample was then irradiated using the same high power light emitting diodes, but with a light intensity of 20 mW cm⁻². The drawing speed of the tensile machine was 0.2 mm min⁻¹. The adhesion strength was estimated as the mean value of five samples (N = 5). Preliminary measurement of tensile shear strength at 40°C was conducted on a Shimpo FGP-50 digital force gauge (Kyoto, Japan) and a self-made hot stage controlled with Omron EM-5N (Kyoto, Japan). The laterally-set specimen was pulled manually using a Sigmakoki Z axis rack and pinion dovetail translation stage (Hidaka, Japan).

Results and Discussion

A hexavalent anthracene compound was successfully synthesised from sorbitol by a two-step reaction. The synthesis scheme and chemical structure are shown in [Figure 1](#). First, all the hydroxyl groups of sorbitol were esterified with 11-bromoundecanoic acid by using a condensation agent.^[19,20] Then, the bromides were replaced with anthracene carboxyl groups to form another ester bond. In this step, 1-, 2-, and 9-anthracene carboxylic acid were used as the reagents in order to investigate effect of the substitute position of terminal anthracene on the physical properties of the products. As already mentioned, adhesive materials should be liquid at room temperature before curing, and such materials could be obtained depending on the substituent position despite the large molecular weights. The obtained compound derived from 2-anthracene was solid at room temperature. In contrast, both compounds from 1- and 9-anthracene were liquid at room temperature, although they had relatively large molecular weights. In the DSC measurements, it could actually be observed that the two liquid compounds exhibited glass transition temperatures below 10°C, and no crystallisation behaviour at room temperature ([Figure 2](#)). These results can be explained by the chemical structure of these molecules. The 2-anthracene derivative has a relatively linear structure, while 1- and 9-anthracene derivatives have bent head structures. It has previously been shown that attaching alkyl tails on a chemical compound often stabilises the compound liquid state.^[21,23] Moreover, liquid mono-anthracene compounds produced by this method have also been previously reported.^[23] Here the point is that one of the causes for the stabilisation of the molecule in the liquid state is the bent shape of the rigid terminal unit. This hypothesis has been confirmed by our azobenzene hexamer, in which the shape change of the terminal phenylazophenoxy group associated with trans to cis photoisomerisation induced a phase transition of the azo hexamer from solid to liquid.^[6] The linear head type of 2-anthracene derivative can be regarded as analog to the solid trans-azobenzene hexamer,

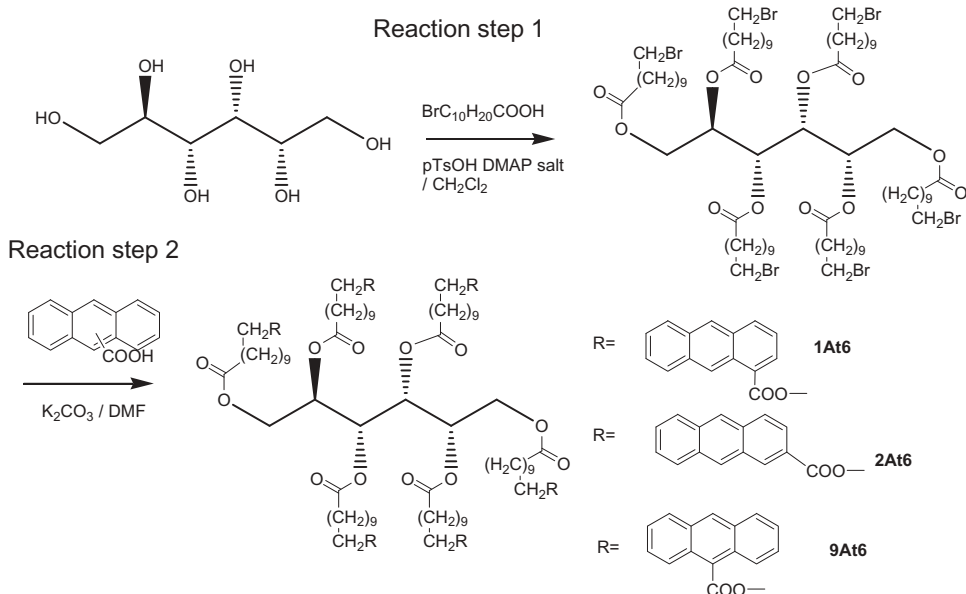


Figure 1. Synthetic scheme of hexavalent anthracene compounds. pTsOH, DMAP and DMF represent p-toluene sulfonyl acid, N,N-dimethylaminopyridine and N, N-dimethylformamide, respectively.

while the bent head type of 1-and 9-anthracene hexamers are analog to the liquid cis-azobenzene hexamer.

To follow the photochemical reaction of the liquid anthracene derivatives, absorption spectra measurements were performed in a thin bulk sample of the 9-anthracene hexamer (Figure 3). The compound exhibited a typical absorption spectrum with a vibrating structure of 9-anthracene carboxylate. Upon irradiation with 405-nm light (2.5 J cm^{-2}), the absorbance at 300–400 nm decreased to 40% as the material changed from liquid to solid. Nevertheless, the initial absorbance was recovered by heating at 180°C for 5 min. This reversible spectrum change corresponds to the photodimerisation of anthracenes and thermal cleavage of the formed dimers. This reaction cycle was repeated 5 times to confirm its reproducibility (Figure 4). The other liquid compound, the 1-anthracene derivative, also has an absorption band at 300–430 nm, without a distinct vibrational structure. Irradiation of the thin film prepared from the 1-anthracene derivative with light at a wavelength of 405 nm (2.5 J cm^{-2}) reduced the absorbance to 55%. In this case, heating of the irradiated sample at 180°C for 5 min resulted in a recovery of 75% of the initial absorbance, in contrast to the complete recovery of 9-anthracene at the same temperature. Longer heating times at 180°C did not affect the absorbance further. However, heating at 220°C for 10 min resulted in a complete recovery of the absorbance. This reaction cycle was also reproducible up to at least 5 cycles (Figure 4). In this experiment, the heating

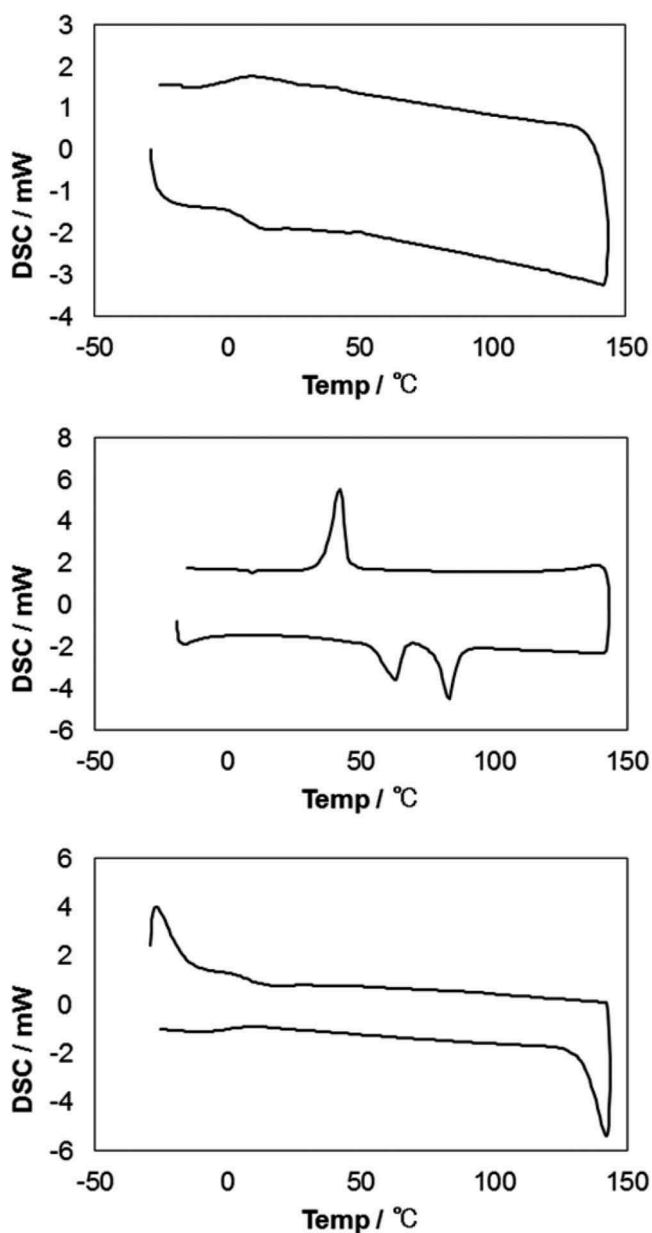


Figure 2. DSC curve of 1At6 (upper), 2At6 (middle) and 9At6 (lower) for the 3rd scan, where the scan rate was 10°C min⁻¹.

time was doubled from 10 min to 20 min to ensure a complete return reaction. Figure 5 shows the heating temperature dependences of the thermal cleavage of sufficiently photoirradiated 1At6 and 9At6. Here, the recovering ratios represent the absorbance at $\lambda_{\text{max}} = 386$ nm after the irradiation or heating process with respect to the initial value. According to the heating temperature used, the recovering ratio can reach different saturated values. It

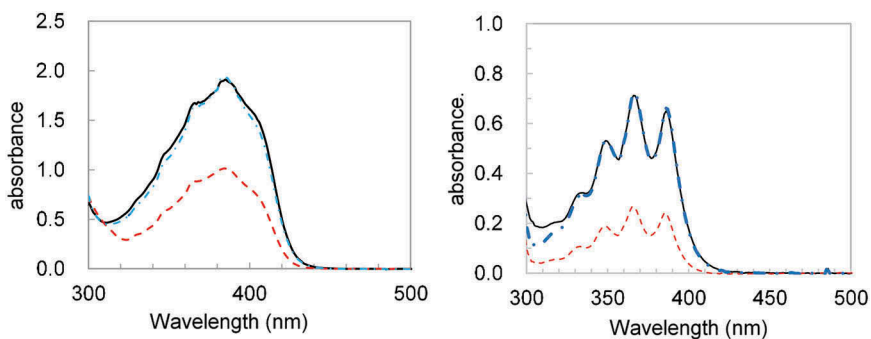


Figure 3. Absorption spectra of 1At6 (left) and 9At6 (right) thin layers before (black solid line) and after irradiation with 405 nm light of ca. 2.5 J cm^{-2} (red dash line) and after heating at 180°C for 10 min (right; blue dashed dotted line) and 220°C for 20 min (left; blue dashed dotted line).

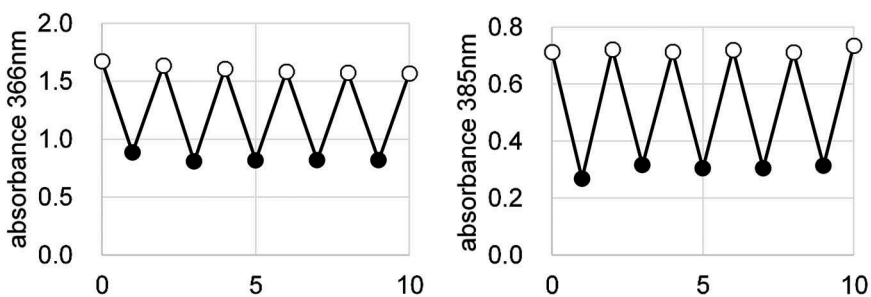


Figure 4. Repetition of photodimerisation and their thermal back reaction of 1At6 (left) and 9At6 (right) on irradiation with 405 nm light of ca. 2.5 J cm^{-2} (closed circle) and on heating at 180°C for 10 min (right; open circle) and 220°C for 20 min (left; open circle), where the first open circles represent initial state and lateral axis indicates the number of total operation of irradiation and heating.

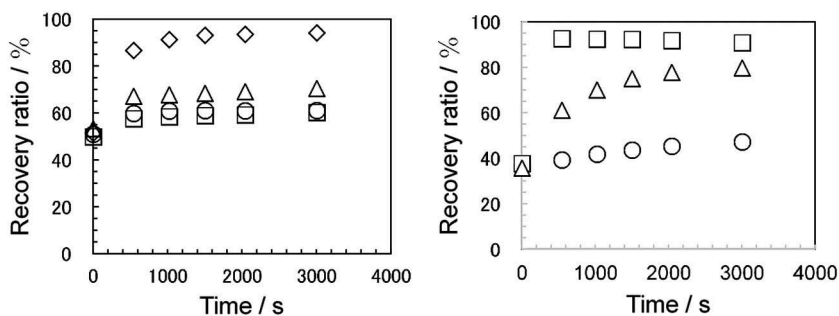


Figure 5. Thermal back reaction of 1At6 (left) and 9At6 (right) photodimers in films on heating at 120°C (circle), 160°C (rectangle), 180°C (triangle) and 220°C (rhomboid).

is reasonable to expect that photodimerisation of substituted anthracenes would intrinsically form multiple stereo isomers with different thermal stabilities, due to different steric hindrances. For instance, the photodimers of 9-anthrance carboxylate have mainly two isomers, head-to-head and head-

to-tail dimers. The head-to-head dimers are less thermally stable than the head-to-tail dimers because of the large steric hindrance in the former.^[9,10] The current compounds contain six anthracene units per molecule. Therefore, the crosslinking structure can remain even after thermal cleavage of the corresponding photodimers. The thermal stability of crosslinked anthracene-hexamers depends on the dissociation temperature of the most stable isomers. The dissociation temperatures were 220°C and 160°C for 1At6 and 9At6, respectively. The dimers of 9At6 showed slow thermal cleavage at 160°C. Thus, the temperature of 180°C was used for heating in other experiments.

In order to investigate the properties of the liquid anthracenes as adhesives, an adhesion strength test was conducted using single lap joint specimens, composed of two glass substrates with a thin film of the sample material in between (Figure 6). Although the liquid anthracenes were initially applied directly to the glass substrates, their application on large adhesion areas was difficult due to their low fluidity. It can be concluded from the dynamic viscoelastic measurements of the liquid anthracenes shown in Figure 7 that the rapid increase of the storage and loss modulus near ambient temperature occurred when cooling from 150°C to room temperature (25°C). These results indicate that these materials are highly viscous liquids at ambient temperature (25°C). In fact, neat liquid anthracenes did not function as reworkable adhesives. For example, although the glass plates with the bulk 9At6 were tightly fixed when irradiated with 405-nm light (>3MPa, materials failure), they were not separated with a tensile strength below 0.2 MPa after heating above 180°C and cooling to room temperature, where the 180°C is the temperature at which the material should be liquefied (Figure 6). The adhesion strength of the sample at a controlled temperature was measured using the preliminary experimental method shown in Figure 8. The glass plates actually sild each other at 40°C at a stress of 2.0 N or less. It was corresponding to <0.05MPa of adhesion strength, which assured de-

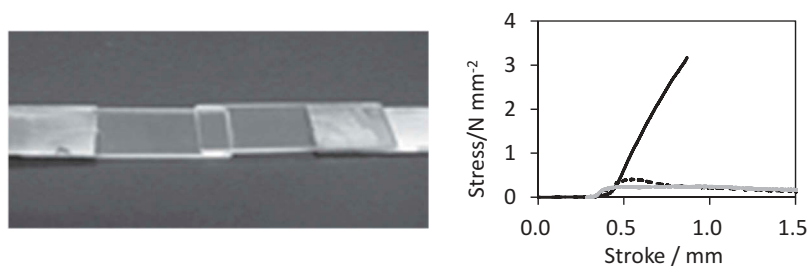


Figure 6. Adhesion strength of single LAP joint specimens composed of two glass substrates with 9At6 in between, before (gray solid line) and after irradiation with 405 nm-light (upper image, black solid line), and after heating at 180°C (dash line), where the stress was normalised with dividing by the initial bond area and measurement was conducted at room temperature.

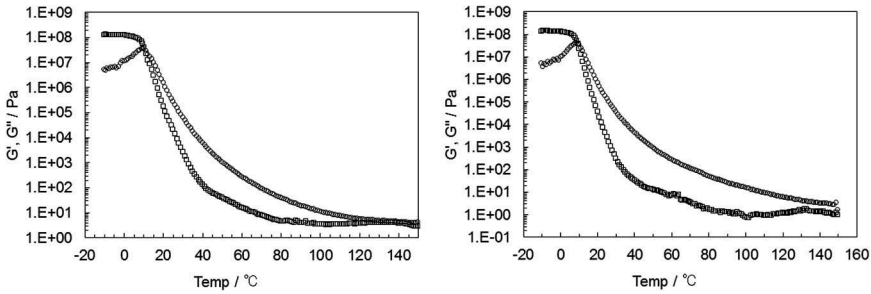


Figure 7. Changes in storage, G' , (rectangle) and loss modulus, G'' , (circle) of 1At6 (left) and 9At6 (right) on cooling process from 150 to -10°C .

crosslinking. In this case the high viscosity of the liquid at room temperature generate adhesion force as pressure sensitive adhesives.

In order to overcome these problems, a typical plasticizer, dibutyl phthalate, was added to the 9-anthracene derivative at 25 wt.%. The mixture was successfully applied to the glass substrates at ambient temperature (Figure 9 left), and was curable by irradiation with 405 nm light, similarly to the photocuring of the neat materials. The glass plates were fixed to each other using the solidified adhesive compound by the photodimerisation of the anthracene unit. Single lap shear tests were performed in order to estimate the adhesion strength. However, it could not be accurately determined because the glass substrates broke at >3 MPa for half of the specimens, before adhesion failure occurred. For the other half of the specimens, an interfacial failure was observed on the surface, where the two plates were separated at 3 MPa. The residual photo-cured adhesives remaining on the surface could easily be peeled from the glass substrate as free standing films (Figure 9 right). In order to investigate the reworkability of the mixture of the anthracene derivatives and the plasticizer, the specimens were heated at 180°C for 5 min. During these experiments, no stress due to the recovery of the fluidic liquid state of the mixture was observed

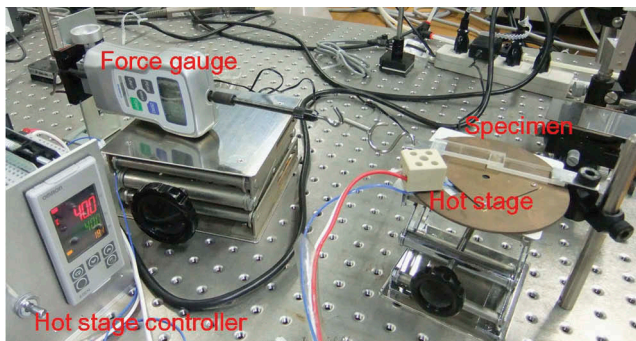


Figure 8. Setup for preliminary measurement of tensile shear strength under controlled temperature (40°C).

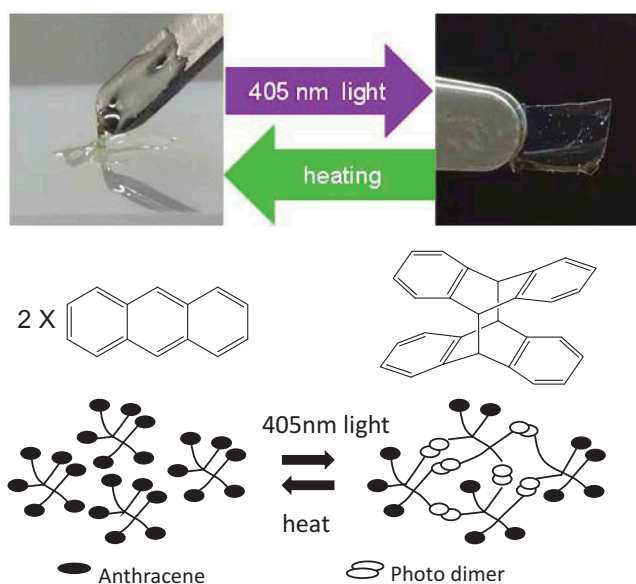


Figure 9. Reversible photocuring of 9At6 with 25% of dibutyl phthalate on irradiation with 405 nm light and on heating 180°C (initial).

on the single lap shear tests at ambient temperature. The same behaviour of the liquefied sample was observed after five cycles of photoirradiation and heating, where the mixture sample was able to be cured and liquefied repeatedly between the two glass plates.

The bonding and debonding ability of 1At6 with 25 wt.% of butyl phthalate was investigated using an experimental setup similar to that of the 9At6 mixture. After irradiation with light at 405 nm for 5 min, the two glass substrates were fixed tightly by the cured 1At6. However, material failure was observed on the lap shear test. After heating at 220°C for 10 min, the cured compound became fluidic, but the fluidity was lost when it was cooled to ambient temperature. The fluidity change indicates that the crosslinking structure was first formed by photoirradiation, and disappeared after the heating process. However, the initial hexamer was not recovered after heating. Similarly, the fluidity of the 9At6 mixture at ambient temperature lost after heating at 220°C, although the NMR spectra were unchanged before and after heating at 220°C for 1 h (Figure 10). One possibility for this decrease in fluidity is that a small amount of thermally degraded, oxidised or ester-exchanged species appears, which increases the viscosity of the materials. These results could be caused by an unknown thermal effect that is enhanced by heating at higher temperatures than 180°C. A study to reveal the unknown effect is now in progress.

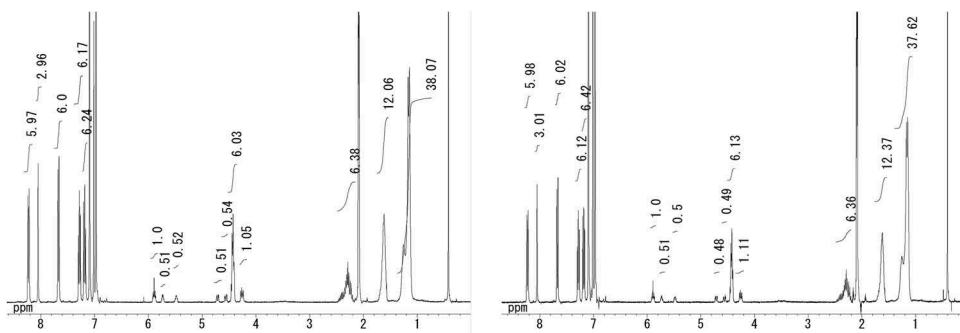


Figure 10. NMR spectra of 9At6 directly dissolved in toluene-d8 (left) and heated at 220°C for 1 h between two glass plates before dissolving it in toluene-d8 (right).

Conclusions

Hexavalent anthracene compounds were successfully synthesised in a two-step reaction, which could be used as reversible adhesives. Among them, it was observed that the compounds with rigid bent terminals were liquid, whereas the linear head compounds were solid at a room temperature. Thus, the stable state of materials of the same composition can be controlled by changing the shape of the molecular terminal. The liquid anthracenes are curable via photodimerisation by irradiation with 405 nm light. The cured state in the case of 9At6 is stable at 120°C, which satisfies the requirements for thermal stability of commonly used adhesives. When the photocured sample is heated above 160°C, the monomeric anthracenes recover and the material returns to its liquid state. However, there were problems regarding the sticky nature of the neat liquid hexamer, which makes it hard to handle as adhesive or coating material. This problem was tackled by adding a typical plasticizer to the compound. The liquid composite with plasticizer can be directly deposited on a substrate, and works as an adhesive for glass plates when it is hardened by light irradiation. The cycle of photoinduced bonding and thermal debonding of the glass substrates is repeatable for at least five times. Although the materials are pale yellow instead of colourless, the bondline is generally thin enough to appear colourless. This is a positive achievement in the field, since colourless transparent adhesives can expand the application area for such reversible and reworkable adhesives.

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References

- [1] Banea, M. D.; Da Silva, L. F. M.; Carbas, R. J. C. Debonding on Command of Adhesive Joints for the Automotive Industry. *Int. J. Adhes. Adhesives*. 2015, **59**, 14–20. DOI: [10.1016/j.ijadhadh.2015.01.014](https://doi.org/10.1016/j.ijadhadh.2015.01.014).
- [2] Hutchinson, A.; Lui, Y.; Lu, Y. Overview of Disbonding Technologies for Adhesive Bonded Joints. *J. Adhes.* 2017, **93**, 737–755. DOI: [10.1080/00218464.2016.1237876](https://doi.org/10.1080/00218464.2016.1237876).
- [3] Ishikawa, H.; Seto, K.; Shimotuma, S.; Kishi, N.; Sato, C. Bond Strength and Disbonding Behavior of Elastomer and Emulsion-Type Dismantlable Adhesives Used for Building Materials. *Int. J. Adhes. Adhes.* 2005, **25**, 193–199. DOI: [10.1016/j.ijadhadh.2004.06.005](https://doi.org/10.1016/j.ijadhadh.2004.06.005).
- [4] Akiyama, H.; Yoshida, M. Photochemically Reversible Liquefaction and Solidification of Single Compounds Based on a Sugar Alcohol Scaffold with Multi Azo-Arms. *Adv. Mater.* 2012, **24**, 2353–2356. DOI: [10.1002/adma.201104880](https://doi.org/10.1002/adma.201104880).
- [5] Akiyama, H.; Kanazawa, S.; Okuyama, Y.; Yoshida, M.; Kihara, H.; Nagai, H.; Norikane, Y.; Azumi, R. Photochemically Reversible Liquefaction and Solidification of Multiazobenzene Sugar-Alcohol Derivatives and Application to Reworkable Adhesives. *ACS Appl. Mater. Interfaces*. 2014, **6**, 7933–7941. DOI: [10.1021/am501227y](https://doi.org/10.1021/am501227y).
- [6] Akiyama, H.; Kanazawa, S.; Yoshida, M.; Kihara, H.; Nagai, H.; Norikane, Y.; Azumi, R. Photochemical Liquid–Solid Transitions in Multi-Dye Compounds. *Mol. Cryst. Liq. Cryst.* 2014, **604**, 64–70. DOI: [10.1080/15421406.2014.967743](https://doi.org/10.1080/15421406.2014.967743).
- [7] Akiyama, H.; Yoshida, M.; Kihara, H.; Norikane, Y.; Azumi, R. Organic Photofunctional Materials Composed of Azobenzene Derivatives: Liquid-Solid Phase Transition in Multi Azobenzene Compounds with Partially Substituted Structures. *J. Photopolym. Sci. Technol.* 2014, **27**, 301–305. DOI: [10.2494/photopolymer.27.301](https://doi.org/10.2494/photopolymer.27.301).
- [8] Akiyama, H.; Yoshida, M.; Kihara, H. Reworkable Adhesives Composed of Photoresponsive Azobenzene Polymer for Glass Substrates. *J. Adhes.* 2017, **93**, 823–830. DOI: [10.1080/00218464.2016.1219255](https://doi.org/10.1080/00218464.2016.1219255).
- [9] Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P.; Lapouyade, R. Photodimerization of Anthracenes in Fluid Solutions: (Part 2) Mechanistic Aspects of the Photocycloaddition and of the Photochemical and Thermal Cleavage. *Chem. Soc. Rev.* 2001, **30**, 248–263. DOI: [10.1039/b006013p](https://doi.org/10.1039/b006013p).
- [10] Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P.; Lapouyade, R. Photodimerization of Anthracenes in Fluid Solution: Structural Aspects. *Chem. Soc. Rev.* 2000, **29**, 43–55. DOI: [10.1039/a801821i](https://doi.org/10.1039/a801821i).
- [11] Becker, H. D.; Unimolecular Photochemistry of Anthracenes. *Chem. Rev.* 1993, **93**, 145–172. DOI: [10.1021/cr00017a008](https://doi.org/10.1021/cr00017a008).
- [12] Kihara, H.; Yoshida, M. Reversible Bulk-Phase Change of Anthrolyl Compounds for Photopatterning Based on Photodimerization in the Molten State and Thermal Back Reaction. *ACS Appl. Mater. Interfaces*. 2013, **5**, 2650–2657. DOI: [10.1021/am400111q](https://doi.org/10.1021/am400111q).
- [13] Chen, W.; Wang, J.-Y.; Zhao, W.; Li, L.; Wei, X. Y.; Balazs, A. C.; Matyjaszewski, K.; Russell, T. P. *J. Am. Chem. Soc.* 2011, **133**, 17217–17224. DOI: [10.1021/ja2036964](https://doi.org/10.1021/ja2036964).
- [14] Saito, S.; Nobusue, S.; Tsuzaka, E.; Yuan, C. X.; Mori, C.; Hara, M.; Seki, T.; Camacho, C.; Irle, S.; Yamaguchi, S. *Nat. Commun.* 2016, **7**. DOI: [10.1038/ncomms12094](https://doi.org/10.1038/ncomms12094).
- [15] Radl, S.; Kreimer, M.; Griesser, T.; Oesterreicher, A.; Moser, A.; Kern, W.; Schlogl, S. New Strategies Towards Reversible and Mendable Epoxy Based Materials Employing [4 π s+4 π s] Photocycloaddition and Thermal Cycloreversion of Pendant Anthracene Groups. *Polym.* 2015, **80**, 76–87. DOI: [10.1016/j.polymer.2015.10.043](https://doi.org/10.1016/j.polymer.2015.10.043).

- [16] Connal, L. A.; Vestberg, R.; Hawker, C. J.; Qiao, G. G. Fabrication of Reversibly Crosslinkable, 3-Dimensionally Conformal Polymeric Microstructures. *Adv. Funct. Mater.* 2008, **18**, 3315–3322. DOI: [10.1002/adfm.v18:20](https://doi.org/10.1002/adfm.v18:20).
- [17] Radl, S. V.; Roth, M.; Gassner, M.; Wolfberger, A.; Lang, A.; Hirschmann, B.; Trimmel, G.; Kern, W.; Griesser, T. Photo-Induced Crosslinking and Thermal De-Crosslinking in Polynorbornenes Bearing Pendant Anthracene Groups. *Eur. Polym. J.* 2014, **52**, 98–104. DOI: [10.1016/j.eurpolymj.2013.10.024](https://doi.org/10.1016/j.eurpolymj.2013.10.024).
- [18] Lopez-Vilanova, L.; Martinez, I.; Corrales, T.; Catalina, F. *Polym. J.* 2014, **56**, 69–76.
- [19] Dincalp, H.; Kizilok, S.; Icli, S. Fluorescent Macromolecular Perylene Diimides Containing Pyrene or Indole Units in Bay Positions. *Dyes Pigments.* 2010, **86**, 32–41. DOI: [10.1016/j.dyepig.2009.11.005](https://doi.org/10.1016/j.dyepig.2009.11.005).
- [20] Strauch, R. C.; Mastarone, D. J.; Sukerkar, P. A.; Song, Y.; Ipsaro, J. J.; Meade, T. J. Reporter Protein-Targeted Probes for Magnetic Resonance Imaging. *Jacs.* 2011, **133**, 16346–16349. DOI: [10.1021/ja206134b](https://doi.org/10.1021/ja206134b).
- [21] Nakanishi, T.; Room Temperature Liquid Formulation by Attaching Alkyl Chains on π -Conjugated Molecules. *J. Synth. Org. Chem. Jpn.* 2014, **72**, 1265–1270. DOI: [10.5059/yukigoseikyokaishi.72.1265](https://doi.org/10.5059/yukigoseikyokaishi.72.1265).
- [22] Babu, S. S.; Nakanishi, T. Nonvolatile Functional Molecular Liquids. *Chem. Commun.* 2013, **49**, 9373–9382. DOI: [10.1039/c3cc45192e](https://doi.org/10.1039/c3cc45192e).
- [23] Babu, S. S.; Hollamby, M. J.; Aimi, J.; Ozawa, H.; Saeki, A.; Seki, S.; Kobayashi, K.; Hagiwara, K.; Yoshizawa, M.; Mohwald, H.; Nakanishi, T. Nonvolatile Liquid Anthracenes for Facile Full-Colour Luminescence Tuning at Single Blue-Light Excitation. *Nat. Commun.* 2013, **4**. DOI: [10.1038/ncomms2969](https://doi.org/10.1038/ncomms2969).