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Rapid Screening Method for Thermal Conductivity Property of Thermal Insulation Materials by Thermochemiluminescent Probe

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Experimental section

Chemicals and materials. All chemicals were purchased from Huawei Ruike Chemical Co. Ltd (Beijing, China). Deionized water (18.2 MU cm, Milli Q, Millipore, Barnstead, CA, USA) was obtained from a Millipore water purification system and was used throughout the experiments. The extruded polystyrene thermal insulation board samples, the expanded polystyrene samples, the polyurethane samples and the ethylene propylene diene monomer rubber-plastic composites were obtained from Zhengya Insulation Material Co. Ltd (Beijing, China).

Apparatus. The CL signals were obtained by an ultra-weak biophysics chemiluminescence (BPCL) analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China). The ^{1}H NMR spectra were recorded on the 400 MHz Bruker ARX400. The ^{13}C NMR spectra were recorded on the Bruker 101 MHz spectrometer at room temperature. $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) was used as the internal standard. Digital photo was obtained on D7000 Nikon.

Synthesis of compound 1. The synthetic approach was shown in Fig. S1. A solution of 9(10H)-acridanone (1.0 g, 5.12 mmol) in N,N-dimethylformamide (DMF, 20 mL) was added to a suspension of NaH (0.15 g, 6.06 mmol) (97%) in dry DMF (10 mL). The mixture was stirred for 30 min at room temperature. After cooling to 0 °C, ethyl 2-bromoacetate (1.28 g, 7.66 mmol) and tetrabutylammonium iodide (20 mg, 0.054 mmol) were added. The solution was stirred for another 24 h at room temperature and then poured into 25 mL of cold water. The precipitate was collected by filtration, dried under vacuum, and purified by flash chromatography on silica gel using 9:1 (v/v) dichloromethane/ethyl acetate as the eluent. Compound 1 was obtained as a pale-yellow solid (0.87 g, 3.1 mmol, yield 60%). ^{1}H NMR (400 MHz, CDCl3): δ 1.31 (t, 3H, J = 7.2 Hz), 4.33 (q, 2H, J = 7.2 Hz), 5.08 (s, 2H), 7.32−7.37 (m, 4H), 7.72−7.76 (m, 2H), 8.58−8.60 (m, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 14.1, 48.4, 62.1, 114.2, 121.8, 122.6, 127.9, 134.0, 142.2, 168.3, 178.1.

Synthesis of compound 2. A solution of 1 (0.25 g, 0.90 mmol) and adamantanone (0.13 g, 0.90 mmol) in dry tetrahydrofuran (THF; 12 mL) was added dropwise to a suspension of $TiCl_4$ (1.18 mmol), THF (1.0 g, 2.70 mmol) and zinc powder (0.18 g, 2.70 mmol) in dry THF (3.0 mL) over a period of 30 min. The reaction mixture was heated at reflux for 4 h, cooled to room temperature, and then filtered over silica gel. Silica was washed with ethyl acetate (50 mL), and the filtrate was evaporated in vacuum. The crude product was purified by flash chromatography on silica gel using 1:1 (v/v) dichloromethane/hexane as the eluent. Compound 2 was obtained as a white solid (0.31 g, 0.78 mmol, yield 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (t, 3H, J = 7.2 Hz), 1.31− 2.19 (m, 12H), 3.46 (s, 2H), 4.28 (q, 2H, J = 7.2 Hz), 4.66 (s, 2H), 6.79 (d, 2H, J = 8.4 Hz), 7.01 (t, 2H, J = 7.6 Hz), 7.15− 7.19 (m, 2H), 7.24−7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 25.0, 32.1, 37.1, 48.7, 61.3, 112.3, 120.0, 120.5, 126.1, 126.2, 127.4, 143.1, 144.7, 169.8.

Synthesis of acridine-based 1,2-dioxetane. Compound 2 (0.1 g, 0.25 mmol) was dissolved in CH_2Cl_2 (10 mL), then methylene blue (1.5 mg, 0.005 mmol) was added. The solution was cooled to -20 °C in an acetone/dry ice bath. The solution was bubbled with oxygen and irradiated for about 5 h under stirring using a 500 W halogen lamp equipped with a UV cut-off filter (0.5% transmission at 400 nm). The reaction product was purified by flash chromatography on silica gel using dichloromethane as the eluent. Acridine-based 1,2-dioxetane was obtained as a yellow solid (0.07 g, 0.16 mmol, yield 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.64 (d, 2H, J = 12.8 Hz), 1.17 (d, 2H, J = 11.6 Hz), 1.28 (t, 3H, J = 7.2 Hz), 1.39−2.11 (m, 8H), 2.29 (s, 2H), 4.29 (q, 2H, J = 7.2 Hz), 4.66 (s, 2H), 6.83 (d, 2H, J = 8.4 Hz), 7.21 (t, 2H, J = 7.6 Hz), 7.36−7.40 (m, 2H), 8.22−8.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 17.4, 25.50, 25.7, 26.9, 31.7, 32.9, 36.1, 39.3, 48.4, 61.6, 86.8, 97.8, 111.8, 121.0, 121.6, 128.4, 129.1, 139.3, 169.3.

TCL measurements. All TCL measurements were implemented with a BPCL analyzer. In order to keep the sample at a given temperature, a temperature control device based on the programmable logic controller (PLC) were built (Fig. S2). The heating element (12 V, 6 W) was comprised of the nickel-chrome serpentine heater. Subsequently, the heating element was bonded with a glass plate, which was used to place the sample. The heating element is powered by a voltage regulator. The accuracy of the temperature control system was adjusted to ± 1 ℃.

Resolution of the TCL probe. Based on the calibration curve for temperature by using the TCL probe, the resolution of the TCL probe (R) could be expressed as

$$R = \Delta y/582.91,$$

where Δy was the minimum detectable TCL signal change. The baseline noise of the TCL probe was 6. Then, Δy was 18 ($S/N = 3$). Finally, we could calculate the resolution of the TCL probe was 0.03 ℃.

Supporting Figures

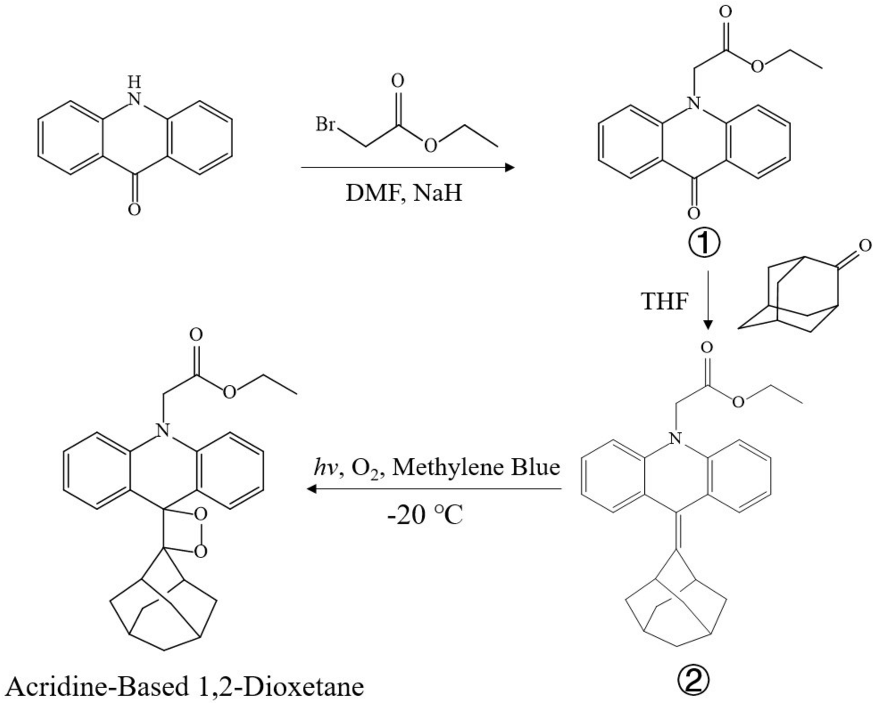

Fig. S1 A three-step synthetic approach to acridine-based 1,2-dioxetane.

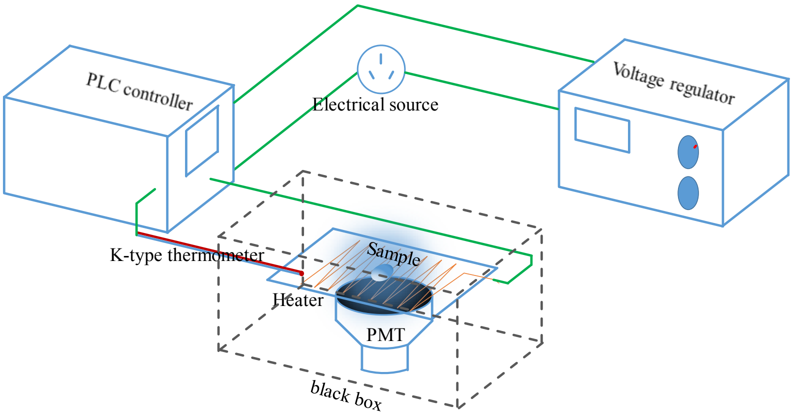

Fig. S2 Schematic diagram of PLC temperature control device.

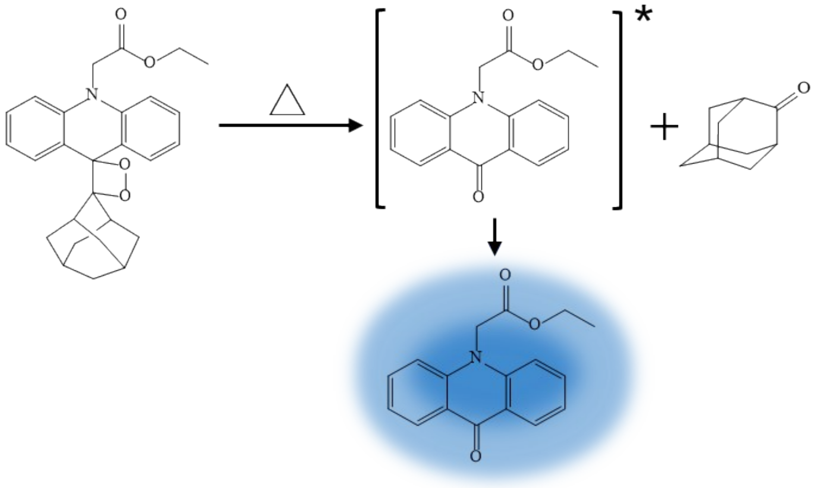

Fig. S3 Schematic diagram of TCL mechanism of acridine-based 1,2-dioxetane.

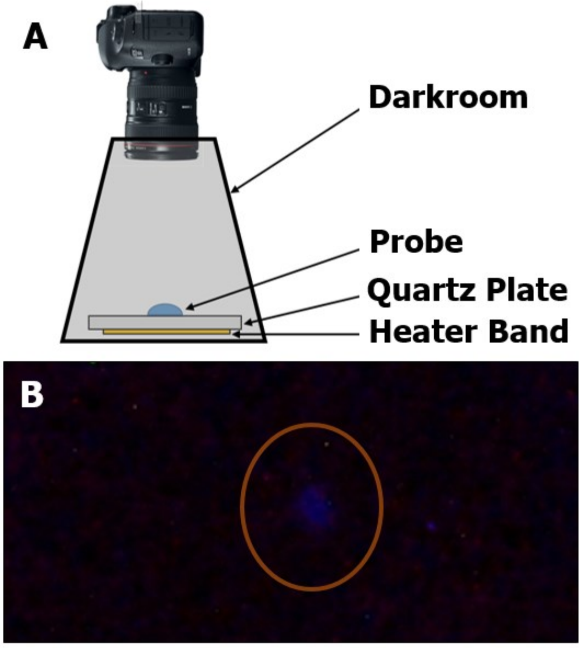

Fig. S4 (A) Schematic diagram of the device for recording the TCL emission image of acridine-based 1,2-dioxetane; (B) The TCL emission image of acridine-based 1,2-dioxetane.

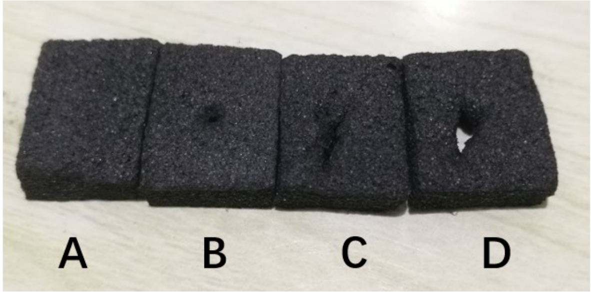

Fig. S5 The photo of the ethylene propylene diene monomer rubber-plastic composite-based undamaged sample (A), the piercing hole sample (B), the cut sample (C) and the defective hole sample (D).

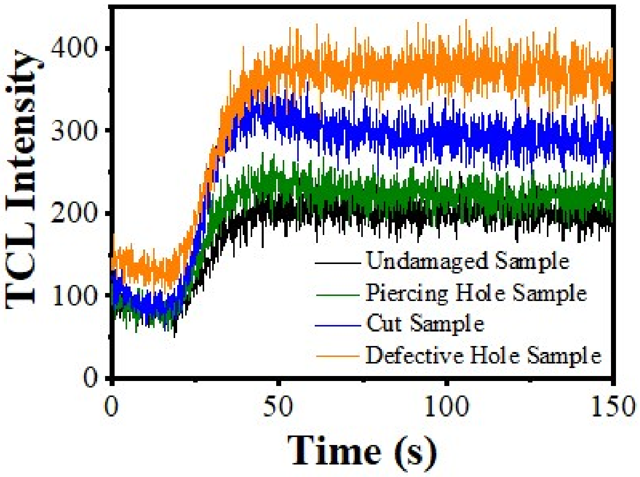

Fig. S6 TCL intensities of acridine-based 1,2-dioxetane on the surface of different ethylene propylene diene monomer rubber-plastic composites.

Table S1. Comparison of luminescent probes for temperature sensing.

Probe (or sensor)	**Useful T range (℃)**	**Ex./Em.**	**Max. sensitivity[a] (% ℃$^{-1}$)**	**Ref.**
$Ru(phen)_3$	0–120	470/580	-2.0[c]	*Adv. Mater.*, 1999, 11, 1296-1299
$Ir(ppy)_2$(carbac)	1–50	405/519	-0.4[b]	*Analyst*, 2010, 135, 1224-1229
$Eu(TTA)_3$	1–50	377/615	-4.28[b]/-1.8[c]	*Rev. Sci. Instrum.*, 2004, 75, 192
$Eu(benzac)_3(phen)$	5–55	381/611	4.0[d]	*Anal. Chem.*, 2011, 83, 2434-2437
$Tb(HFA)_3(H_2O)_2$	10–50	363/543	-1.80[b]	*Chem. Phys. Lett.*, 2004, 398, 500-504
$Tb(HFA)_3(TPPO)_2$	10–50	345/543	-1.90[b]	*Chem. Phys. Lett.*, 2004, 398, 500-504
Poly(NIPAM-co-HC)	25–40	510/580	+500[a]	*Langmuir*, 2008, 24, 4273-4279
Poly(NIPAM-co-BODIPY)	23–35	490/600	+83[a]	*Langmuir*, 2009, 25, 13176-13182
Poly(NIPMAM-co-DBD-AE)	45–54	444/556	+79[a]	*Anal. Chem.*, 2003, 75, 5926-5935
Poly(NNPAM-co-DBD-AE)	29–37	444/563	+266[a]	*Anal. Chem.*, 2003, 75, 5926-5935
Poly(NIPAM-co-DBD-AE)	18–24	444/566	+166[a]	*Anal. Chem.*, 2003, 75, 5926-5935
Acridine-based 1,2-dioxetane	85–130	–/465	+2.2	Our work

[a] The maximum sensitivity is not always ensured over the whole working range. [b] Intensity signal change. [c] Lifetime signal change. [d] Ratiometric signal change.