Supporting Information

for

Click chemistry towards thermally reversible photochromic 4,5-bisthiazolyl-1,2,3-triazoles

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Additional experimental data and spectra
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SI-1. Experimental Details

General.

Chemical reactions were carried out under a dry nitrogen atmosphere. All solvents were used as received. All flash column chromatography purifications were carried out on 230–400 mesh silica gel using ethyl acetate and hexane or chloroform and hexane as eluent. Analytical thin-layer chromatography was performed on the pre-coated 0.25-mm thick silica gel TLC plates. 

$^1$H NMR Spectra were recorded in deuteriochloroform (CDCl₃) with a 300 MHz NMR spectrometer. $J$ values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Infrared spectra (IR) were recorded on a FTIR spectrometer. Low- and high-resolution mass spectra were measured by the electron ionization mass spectrometry using a Mass spectrometer. Ultraviolet and visible spectra were recorded on a UV–vis spectrophotometer equipped with a photodiode array detector and a temperature-controllable cell holder. Melting points were measured using a hot stage microscope, and those were uncorrected.

Photochemical reactions were all carried out in a 10 mm path length quartz cell. Photoirradiation with 313 nm light was carried out using a 500 W high-pressure mercury lamp, separated by filters (a 5 cm water filter, a UV-D35 glass filter, a 5 cm aqueous NiSO₄·6H₂O solution, a 1 cm aqueous K₂CrO₄ solution, and a 1 cm aqueous potassium diphthalate solution). High-performance liquid chromatography (HPLC) equipped with a UV–vis detector and a silica gel column (20 mm diameter × 250 mm) with chloroform/hexane as the eluent was used for the purification of synthesized compounds.
Synthetic schemes of 4,5-bisthiazolyl-1,2,3-triazoles.

Synthesis of 1o, 2o, and 3o were carried out according to the following procedures.

3) Commercially available.
Synthesis of 4,4'-([1-benzyl-1H]1,2,3-triazole-4,5-diyl)bis(5-methyl-2-phenylthiazole) (10)

A mixture of 1,2-bis(5-methyl-2-phenylthiazol-4-yl)ethyne (11, 202.1 mg, 0.543 mmol, 1.0 equiv), benzyl azide (0.560 mL, 4.48 mmol, 8.28 equiv), Cp*RuCl(PPh3)2 (56.6 mg, 0.0711 mmol, 0.13 equiv) and 1,4-dioxane (4.00 mL) was refluxed for 43 h under a N2 atmosphere with vigorous stirring. The solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (15%) as the eluent, to give 98.6 mg (0.195 mmol) of 4,4'-([1-benzyl-1H]1,2,3-triazole-4,5-diyl)bis(5-methyl-2-phenylthiazole) 10 as a pale yellow solid in 36% yield.

1H NMR (300 MHz, CDCl3, TMS) δ/ppm 1.83 (3H, s), 2.73 (3H, s), 5.70 (2H, s), 7.04-7.07 (2H, m), 7.20-7.23 (3H, m), 7.31-7.33 (3H, m), 7.46-7.48 (3H, m), 7.66-7.69 (2H, m), 7.94-7.97 (2H, m).

LRMS (EI, 70 eV) m/z (rel intensity), 505 (M+, 75), 477 ((M-Na)+, 100), 386 ((M-119)+, 63).

IR (neat) v/cm⁻¹ 1485, 1456, 1440, 1254, 972, 761, 689.

Found: m/z 505.14133. Calcd for C₂₉H₂₃N₅S₂: M, 505.13950.

Mp 61–64 °C.

Synthesis of 4-iodo-2-(4-methoxyphenyl)-5-methylthiazole (13)

To a solution of 4-bromo-2-(4-methoxyphenyl)-5-methylthiazole (12, 3.2 g, 11 mmol, 1.0 equiv) in anhydrous THF (140 mL) was added dropwise a hexane solution of n-butyllithium (1.63 mol dm⁻³, 8.28 mL, 13 mmol, 1.1 equiv) at −78 °C under a N2 atmosphere. The resulting solution was stirred at this temperature for 40 min, then a solution of I2 (5.144 g, 20 mmol, 1.8 equiv) in anhydrous THF (40 mL) was added through a cannula, and the mixture was stirred for overnight with gradual warming up to room temperature. The reaction was quenched by adding 10% aq. Na₂S₂O₅, and the resultant mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and evaporated. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (5% to 15%) as the eluent, to give 3.47 g (10 mmol) of 4-iodo-2-(4-methoxyphenyl)-5-methylthiazole 13 as a white solid in 93% yield.

1H NMR (300 MHz, CDCl₃, TMS) δ/ppm 2.43 (3H, s), 3.85 (3H, s), 6.92 (2H, d(AA'BB')), J/Hz = 8.9, 7.80 (2H, d(AA'BB')), J/Hz = 9.0).

LRMS (EI, 70 eV) m/z (rel intensity), 331 (M+, 100), 316 ((M-Me)+, 10).

IR (neat) v/cm⁻¹ 3010, 1603, 1516, 1436, 1248, 1170, 1011, 972, 831, 799.

Mp 131–132 °C.

Synthesis of 2-(4-methoxyphenyl)-5-methyl-4-((trimethylsilyl)ethynyl)thiazole (14)

To a solution of 4-iodo-2(4-methoxyphenyl)-5-methylthiazole (13, 1.5 g, 4.5 mmol, 1.0 equiv) in anhydrous THF (50 mL) and triethylamine (50 mL) was added dichlorobis(triphenylphosphine)palladium(II) (158.9 mg, 0.227 mmol, 0.05 equiv) and copper(I)
iodide (43 mg, 0.226 mmol, 0.05 equiv). To the resulting solution was added an excess of trimethylsilylthyne (1.5 mL, 10 mmol, 2.4 equiv) under a N₂ atmosphere, and the mixture was stirred for overnight at room temperature. The reaction was quenched by adding water and 3 mol dm⁻³ HCl aq, and the resultant mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and evaporated. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (0% to 3%) as the eluent, to give 1.248 g (4.14 mmol) of 2-(4'-methoxyphenyl)-5'-methyl-4'-(trimethylsilyl)ethynyl)thiazole (14) as a white solid in 92% yield.

¹H NMR (300 MHz, CDCl₃, TMS) δ/ppm 0.28 (9H, s), 2.54 (3H, s), 3.84 (2H, s), 6.91 (2H, d(AABB'), J/Hz = 8.9), 7.84 (2H, d(AABB'), J/Hz = 9.0).

LRMS (EI, 70 eV) m/z (rel intensity), 301 (M⁺, 100), 286 [(M-Me)⁺, 75].

IR (neat) ν/cm⁻¹ 2961, 2154, 1605, 1307, 1248, 1168, 1101, 1027, 893, 840, 826, 760, 656, 516.

Mp 92–93 °C.

**Synthesis of 4'-ethynyl-2-(4'-methoxyphenyl)-5'-methylthiazole (15)**

A suspension of 2-(4'-methoxyphenyl)-5'-methyl-4'-(trimethylsilyl)ethynyl)thiazole (14, 1.248 g, 4.14 mmol, 1.0 equiv) and K₂CO₃ (3.433 g, 25 mmol, 6 equiv) in methanol (45 mL) and THF (60 mL) was stirred at room temperature for 3 h. The resulting suspension was evaporated to half volume in vacuo. The resultant mixture was poured into water, and the resultant mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (10% to 20%) as the eluent, to give 949.0 mg (4.14 mmol) of 4'-ethynyl-2-(4'-methoxyphenyl)-5'-methylthiazole (15) as a pale yellow solid in quantitative yield.

¹H NMR (300 MHz, CDCl₃, TMS) δ/ppm 2.55 (3H, s), 3.29 (1H, s), 3.85 (3H, s), 6.93 (2H, d(AABB'), J/Hz = 8.9), 7.84 (2H, d(AABB'), J/Hz = 9.0).

LRMS (EI, 70 eV) m/z (rel intensity), 229 (M⁺, 100), 214 [(M-Me)⁺, 13].

IR (neat) ν/cm⁻¹ 3258, 2919, 1605, 1522, 1254, 1171, 1101, 1027, 893, 840, 826, 760, 680, 509.

Mp 136–137 °C.

**Synthesis of 1,2-bis(2-(4'-methoxyphenyl)-5'-methylthiazol-4-yl)ethyne (16)**

A solution of 4'-ethynyl-2-(4'-methoxyphenyl)-5'-methylthiazole (15, 0.80 g, 3.5 mmol, 1.0 equiv) and 4'-iodo-2-(4'-methoxyphenyl)-5'-methylthiazole (13, 1.15 g, 3.5 mmol, 1.0 equiv) in anhydrous THF (10 mL) and triethylamine (10 mL) was treated with dichlorobis(triphosphine)palladium(II) (122.8 mg, 0.175 mmol, 0.05 equiv) and copper(I) iodide (0.02 g, 0.11 mmol, 0.03 equiv). The resulting solution was stirred at room temperature for overnight under a N₂ atmosphere. The reaction was quenched by adding water and 3 mol dm⁻³ HCl aq., and the resultant mixture was extracted with ethyl acetate. The combined
organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and evaporated. The residue was purified by flash column chromatography on silica gel using chloroform/hexane (10% to 30%) as the eluent, to give 28.0 mg (0.065 mmol) of 1,2-bis(2-(4-methoxyphenyl)-5-methylthiazol-4-yl)ethyne (16) as a pale yellow solid in 2% yield.

^1H NMR (300 MHz, CDCl₃, TMS) δ/ppm 2.64 (6H, s), 3.86 (6H, s), 6.95 (4H, d(AA'BB'), J/Hz = 8.9), 8.87 (4H, d(AA'BB'), J/Hz = 8.9).

LRMS (EI, 70 eV) m/z (rel intensity), 432 (M⁺, 100), 216 (M⁺/2, 18).

IR (neat) v/cm⁻¹ 2924, 2851, 1604, 1519, 1432, 1304, 1251, 1172, 1033, 829, 721, 511.

Found: m/z 432.09632 Calcd for C₂₄H₂₀N₂O₂S₂: M, 432.09663.

Mp 224–229 °C.

**Synthesis of 4,4″-(1-benzyl-1H,1,2,3-triazole-4,5-diyl)bis(2-(4-methoxyphenyl)-5-methylthiazole) (20)**

A mixture of 1,2-bis(2-(4-methoxyphenyl)-5-methylthiazol-4-yl)ethyne (16, 25 mg, 0.058 mmol, 1.0 equiv), benzyl azide (0.0435 mL, 0.35 mmol, 6.0 equiv), Cp*RuCl(cod) (6.6 mg, 0.017 mmol, 0.3 equiv), and toluene (2 mL) was stirred at room temperature for 2 days under a N₂ atmosphere. The solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (0% to 30%) as the eluent, to give 17.0 mg (0.031 mmol) of 4,4″-(1-benzyl-1H,1,2,3-triazole-4,5-diyl)bis(2-(4-methoxyphenyl)-5-methylthiazole) (20) as a pale yellow solid in 53% yield.

^1H NMR (300 MHz, CDCl₃, TMS) δ/ppm 1.80 (3H, s), 2.67 (3H, s), 3.81 (3H, s), 3.88 (3H, s) 5.69 (2H, s), 6.84 (2H, d(AA'BB'), J/Hz = 8.9), 6.98 (2H, d(AA'BB'), J/Hz = 9.0), 7.04-7.08 (2H, m), 7.20-7.22 (3H, m), 7.63 (2H, d(AA'BB'), J/Hz = 8.9), 7.84 (2H, d(AA'BB'), J/Hz = 8.9).

LRMS (EI, 70 eV) m/z (rel intensity), 565 (M⁺, 26), 537 (M⁺-N₂)⁺, 100, 446(M⁺-119)⁺, 63.

IR (neat) v/cm⁻¹ 2937, 1607, 1522, 1463, 1306, 1255, 1172, 1033, 832.

Found: m/z 565.17141 Calcd for C₃₁H₁₆N₅O₂S₂: M, 565.16063.

Mp 66–70 °C.

**Synthesis of 2-(4-cyanophenyl)-5-methylthiazole (18)**

A suspension of 2-bromo-5-methylthiazole (17, 2.01 g, 11.3 mmol, 1.00 equiv), p-cyanophenylboronic acid (1.8259 g, 12.4 mmol, 1.10 equiv), Pd(PPh₃)₄ (774.2 mg, 0.676 mmol, 0.06 equiv), and K₂CO₃ (6.3399 g, 45.9 mmol, 4.07 equiv) in THF (40 mL) and water (20 mL) was refluxed for 15 h under a N₂ atmosphere with vigorous stirring. The reaction was quenched by 3 mol dm⁻³ HCl aq., and the resultant mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and evaporated. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (3% to 8%) as the eluent, to give 1.6136 g (8.06 mmol) of 2-(4-cyanophenyl)-5-
methylthiazole (18) as a white solid in 71% yield.

$^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$/ppm 2.55 (3H, d, $J$/Hz = 1.1), 7.58 (1H, q, $J$/Hz = 1.1), 7.71 (2H, d($AA'BB'$), $J$/Hz = 8.7), 7.99 (2H, d($AA'BB'$), $J$/Hz = 8.7).

LRMS (EI, 70 eV) m/z (rel intensity), 200 (M$^+$, 100).

IR (neat) v/cm$^{-1}$ 2924, 1604, 1499, 1432, 1173, 1105, 972, 859, 820, 628, 524.

Mp 118–127 °C.

**Synthesis of 4-bromo-2-(4-cyanophenyl)-5-methylthiazole (19)**

To a solution of 2-(4-cyanophenyl)-5-methylthiazole (18, 1.5757 g, 7.87 mmol, 1.0 equiv) and propylene oxide (0.740 mL, 10.6 mmol, 1.34 equiv) in acetonitrile (100 mL) was added Br$_2$ (0.725 mL, 14.1 mmol, 1.80 equiv) dropwise at 0 °C. After the mixture was stirred for 5.5 h with gradual warming up to room temperature, the reaction was quenched by adding 10% aq. Na$_2$SO$_3$. Then the resultant mixture was extracted with ethyl acetate. The combined organic layer was washed with sat. aq. NaCl, and dried over anhydrous Na$_2$SO$_4$, the drying agent filtered off, and evaporated. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (5% to 6%) as the eluent, to give 1.6653 g (5.97 mmol) of 4-bromo-2-(4-cyanophenyl)-5-methylthiazole (19) as a white solid in 67% yield.

$^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$/ppm 2.48 (3H, s), 7.72 (2H, d($AA'BB'$), $J$/Hz = 8.7), 7.98 (2H, d($AA'BB'$), $J$/Hz = 8.7).

LRMS (EI, 70 eV) m/z (rel intensity), 280 (M$^+$, 100) 278 (M$^+$, 99), 199 (M-Br$^+$, 3), 146 (84), 71 (34).

IR (neat) v/cm$^{-1}$ 3059, 2225, 1605, 1500, 1219, 1173, 1105, 972, 859, 820, 628, 524.

Mp 174–175 °C.

**Synthesis of 2-(4-cyanophenyl)-5-methyl-4-((trimethylsilyl)ethynyl)thiazole (20)**

To a solution of 4-bromo-2-(4-cyanophenyl)-5-methylthiazole (19, 216.6 mg, 0.776 mmol, 1.0 equiv) and trimethylsilylthiophene (0.700 mL, 4.95 mmol, 6.38 equiv) in anhydrous THF (4 mL) and triethylamine (4 mL) was added dichlorobis(triphenylphosphine)palladium(II) (8.6 mg, 0.0123 mmol, 0.016 equiv) and copper(I) iodide (2.3 mg, 0.0121 mmol, 0.016 equiv). The mixture was refluxed for 9 h under a N$_2$ atmosphere with vigorous stirring. The reaction was quenched by adding water and 3 mol dm$^{-3}$ HCl aq, and the resultant mixture was extracted with ethyl acetate. The combined organic layer was washed with sat. aq. NaCl, and dried over anhydrous Na$_2$SO$_4$, the drying agent filtered off, and evaporated. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (2% to 20%) as the eluent, to give 102.6 mg (0.346 mmol) of 2-(4-cyanophenyl)-5-methyl-4-((trimethylsilyl)ethynyl)thiazole (20) as a pale yellow solid in 45% yield.

$^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$/ppm 0.29 (9H, s), 2.59 (3H, s), 7.70 (2H, d($AA'BB'$), $J$/Hz = 8.6), 8.01 (2H, d($AA'BB'$), $J$/Hz = 8.7).
LRRMS (EI, 70 eV) m/z (rel intensity), 296 (M+, 59), 281 ((M-Me)+, 100).
IR (neat) v/cm⁻¹ 2958, 2223, 1770, 1605, 1498, 1247, 1103, 974, 844.

Mp 175–176 °C.

**Synthesis of 4'-ethynyl-2-(4'-cyanophenyl)-5'-methylthiazole (21)**

A mixture of 2-(4'-cyanophenyl)-5'-methyl-4'-((trimethylsilyl)ethynyl)thiazole (20, 90.9 mg, 0.307 mmol, 1.00 equiv) and K₂CO₃ (215.8 mg, 1.56 mmol, 5.09 equiv) in methanol (4 mL) and THF (4 mL) was stirred for overnight at room temperature. The resulting mixture was evaporated to half volume in vacuo. The resultant mixture was poured into water, and the resultant mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (5% to 25%) as the eluent, to give 52.5 mg (0.234 mmol) of 4'-ethynyl-2-(4'-cyanophenyl)-5'-methylthiazole (21) as a light brown solid in 76% yield.

¹H NMR (300 MHz, CDCl₃, TMS) δ/ppm 2.61 (3H, s), 3.34 (1H, s), 7.71 (2H, d(AA'BB'), J/Hz = 8.9), 8.01 (2H, d(AA'BB'), J/Hz = 8.7).

LRRMS (EI, 70 eV) m/z (rel intensity), 224 (M⁺, 100).
IR (neat) v/cm⁻¹ 3300, 2994, 2359, 1769, 1241, 841.

Mp 168–170 °C.

**Synthesis of 1,2-bis(2-(4-cyanophenyl)-5-methylthiazol-4-yl)ethyne (22)**

A mixture of 2-(4'-cyanophenyl)-4'-ethynyl-5'-methylthiazole (21, 180.0 mg, 3.5 mmol, 1.00 equiv), 4'-bromo-2-(4'-cyanophenyl)-5'-methylthiazole (19, 239.6 mg, 0.858 mmol, 1.07 equiv), Pd(MeCN)₂Cl₂ (13.9 mg, 0.0536 mmol, 0.07 equiv), X-Phos (25.8 mg, 0.0541 mmol, 0.07 equiv), and Cs₂CO₃ (686.6 mg, 2.11 mmol, 2.63 equiv), in 15 wt% aq. polyoxyethanol-α-tocopheryl sebacate (0.8 mL), water (3.2 mL), and THF (4.0 mL) was stirred at room temperature for overnight and heated for 1 h under a N₂ atmosphere. The resultant mixture was extracted with chloroform. The combined organic layer was washed with sat. aq. NaCl, and dried over anhydrous Na₂SO₄, the drying agent filtered off, and evaporated. The residue was purified by flash column chromatography on silica gel using chloroform/hexane (40% to 100%) as the eluent, to give 203.0 mg (0.480 mmol) of 1,2-bis(2-(4-cyanophenyl)-5'-methylthiazol-4-yl)ethyne (22) as a pale yellow solid in 60% yield.

¹H NMR (300 MHz, CDCl₃, TMS) δ/ppm 2.70 (6H, s), 7.73 (4H, d(AA'BB'), J/Hz = 8.7), 8.04 (4H, d(AA'BB'), J/Hz = 8.7).

LRRMS (EI, 70 eV) m/z (rel intensity), 422 (M⁺, 100).
IR (neat) v/cm⁻¹ 2919, 2359, 1769, 1604, 972, 841, 542.
Found: m/z 422.06818 Calcd for C₂₄H₁₄N₁₄S₂: M, 422.06599.
Mp 246–249 °C.
Synthesis of 4,4’-(1-benzyl-1H-1,2,3-triazole-4,5-diyl)bis(2-(4-cyanophenyl)-5-methylthiazole) (3o)

A mixture of 1,2-bis(2-(4-cyanophenyl)-5-methylthiazol-4-yl)ethyne (22, 43.8 mg, 0.104 mmol, 1.00 equiv), benzyl azide (0.050 mL, 0.400 mmol, 3.86 equiv), Cp*RuCl(PPh₃)₂ (2.6 mg, 0.00327 mmol, 0.03 equiv), 1,4-dioxane 3.00 mL was stirred at 70 °C for 4.5 h and at 100 °C for 11.5 h under a N₂ atmosphere. The solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (15% to 30%) as eluent, to give a mixture of 3o and 22. Further separation of the mixture of 3o and 22 was carried out with semi-preparative HPLC (silica gel column, 60% chloroform/hexane as the eluent) to afford 11.7 mg (0.0211 mmol) of 4,4’-(1-benzyl-1H-1,2,3-triazole-4,5-diyl)bis(2-(4-cyanophenyl)-5-methylthiazole) (3o) as a white solid in 20% yield.

¹H NMR (300 MHz, CDCl₃, TMS) δ/ppm: 1.86 (3H, s), 2.87 (3H, s), 5.65 (2H, s), 7.01-7.04 (2H, m), 7.22-7.24 (3H, m), 7.59 (2H, d(AAB''), J/Hz = 8.9), 7.70 (2H, d(AA''B''), J/Hz = 8.7), 7.76 (2H, d(AA''B''), J/Hz = 8.7), 8.03 (2H, d(AA''B''), J/Hz = 8.7).

LRMS (EI, 70 eV) m/z (rel intensity), 555 (M⁺, 83), 436 ((M⁺-119)⁺, 82), 91 (100).

IR (neat) v/cm⁻¹: 2923, 2363, 2226, 1604, 1485, 1437, 1022, 975, 838.

Found: m/z 555.11755 Calcd for C₃₁H₂₁N₇S₂: M, 555.12999.

Mp 89–95 °C.
SI-2. Change in absorption spectra of 1o, 2o, and 3o by photochromism

Photoirradiation conditions

Concentration:

1o: $4.44 \times 10^{-5}$ mol dm$^{-3}$
2o: $4.38 \times 10^{-5}$ mol dm$^{-3}$
3o: $4.73 \times 10^{-5}$ mol dm$^{-3}$

Temperature: 28 °C

Irradiation light wavelength: 313 nm
Light intensity: 1.8 mW cm$^{-2}$
Optical path length: 1 cm
Fig. S1: Absorption spectral change of 1o in ethanol (Left: photoirradiation. Right: thermal back reaction)

Fig. S2: Absorption spectral change of 1o in ethyl acetate (Left: photoirradiation. Right: thermal back reaction)

Fig. S3: Absorption spectral change of 1o in toluene (Left: photoirradiation. Right: thermal back reaction)
**Fig. S4:** Absorption spectral change of 2o in ethanol (Left: photoirradiation. Right: thermal back reaction)

**Fig. S5:** Absorption spectral change of 2o in ethyl acetate (Left: photoirradiation. Right: thermal back reaction)

**Fig. S6:** Absorption spectral change of 2o in toluene (Left: photoirradiation. Right: thermal back reaction)
Fig. S7: Absorption spectral change of 3o in ethanol (Left: photoirradiation. Right: thermal back reaction)

Fig. S8: Absorption spectral change of 3o in ethyl acetate (Left: photoirradiation. Right: thermal back reaction)

Fig. S9: Absorption spectral change of 3o in toluene (Left: photoirradiation. Right: thermal back reaction)
SI-3. Analysis of thermal back reactions

Thermal back reaction conditions

Concentration:
10: $4.44 \times 10^{-5}$ mol dm$^{-3}$
20: $1.46 \times 10^{-5}$ mol dm$^{-3}$
30: $9.46 \times 10^{-5}$ mol dm$^{-3}$

Temperature:
10: 20 °C, 25 °C, 30 °C
20: 20 °C, 25 °C, 30 °C
30: 0 °C, 5 °C, 10 °C

Irradiation light wavelength: 313 nm
Light intensity: 1.2 mW cm$^{-2}$
Optical path length: 1 cm

Analysis of thermal back reactions

Thermal back reactions of triazoles were carried out in ethanol, acetonitrile, ethyl acetate and toluene at three different temperatures. The decay curve of absorbance $A_t$ at the absorption maximum wavelength of the compound in each solvent was traced, ln ($A_t/A_0$) was plotted against reaction time $t$, and the rate constant $k$ of the compound at the temperature $T$ was calculated. Then, ln $k$ was plotted against $T^{-1}$ to obtain $A$ (pre-exponential factor) and $E_a$ (Arrhenius activation energy) from the intercept of y-axis and gradient of the first order equation, respectively.
Fig. S10. Thermal back reaction of triazole 1c at various temperatures in (a) EtOH, (b) MeCN, (c) AcOEt, (d) toluene

Top: Absorption spectral change, Bottom: Decay lines of absorption maximum: $A_0 = A_t$ at 810 s

Irradiation time: 10–810 s, Detection wavelength: $\lambda_{\text{max}}$ in each solvent.
Fig. S11. Thermal back reaction of triazole 2c at various temperatures in (a) EtOH, (b) MeCN, (c) AcOEt, (d) toluene

Top: Absorption spectral change, Bottom: Decay lines of absorption maximum: $A_0 = A_t$ at 610 s

Irradiation time: 10–610 s, detection wavelength: $\lambda_{\text{max}}$ in each solvent
Fig. S12. Thermal back reaction of triazole 3c at various temperatures in (a) EtOH, (b) MeCN, (c) AcOEt, (d) toluene

Top: Absorption spectral change, Bottom: Decay lines of absorption maximum: $A_0 = A_t$ at 521 s
Irradiation time: 10–510 s, Detection wavelength: $\lambda_{max}$ in each solvent
Fig. S13. Arrhenius plots. (a) triazole 1c, (b) triazole 2c, (c) triazole 3c.
SI-4. DFT and TD DFT calculation results

Calculation conditions

DFT and TD DFT calculations of 1c–3c were carried out with Spartan’18 software (Wavefunction) at the B3LYP/6-31G* level.

1c

Allowed transitions

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<th>wavelength/nm</th>
<th>strength</th>
<th>MO Component</th>
<th>%</th>
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<td>HOMO-3 -&gt; LUMO</td>
<td>79%</td>
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<td>364.51</td>
<td>0.0497</td>
<td>HOMO-1 -&gt; LUMO</td>
<td>67%</td>
</tr>
<tr>
<td>382.35</td>
<td>0.0314</td>
<td>HOMO -&gt; LUMO+2</td>
<td>95%</td>
</tr>
<tr>
<td>430.24</td>
<td>0.0577</td>
<td>HOMO -&gt; LUMO+1</td>
<td>88%</td>
</tr>
<tr>
<td>704.25</td>
<td>0.4309</td>
<td>HOMO -&gt; LUMO</td>
<td>102%</td>
</tr>
</tbody>
</table>

2c

Allowed transitions

<table>
<thead>
<tr>
<th>wavelength/nm</th>
<th>strength</th>
<th>MO Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>356.88</td>
<td>0.0875</td>
<td>HOMO-3 -&gt; LUMO</td>
<td>65%</td>
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<tr>
<td></td>
<td></td>
<td>HOMO-1 -&gt; LUMO</td>
<td>21%</td>
</tr>
<tr>
<td>359.50</td>
<td>0.0453</td>
<td>HOMO -&gt; LUMO+3</td>
<td>29%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO -&gt; LUMO+6</td>
<td>26%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-1 -&gt; LUMO</td>
<td>22%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-3 -&gt; LUMO</td>
<td>14%</td>
</tr>
<tr>
<td>366.15</td>
<td>0.4453</td>
<td>HOMO-2 -&gt; LUMO</td>
<td>86%</td>
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<tr>
<td>385.83</td>
<td>0.0117</td>
<td>HOMO -&gt; LUMO+2</td>
<td>89%</td>
</tr>
<tr>
<td>Wavelength/nm</td>
<td>Strength</td>
<td>MO Component</td>
<td>%</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>--------------------</td>
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</tr>
<tr>
<td>428.46</td>
<td>0.0596</td>
<td>HOMO -&gt; LUMO+1</td>
<td>84%</td>
</tr>
<tr>
<td>698.93</td>
<td>0.5445</td>
<td>HOMO -&gt; LUMO</td>
<td>102%</td>
</tr>
</tbody>
</table>

3c

### Allowed transitions

<table>
<thead>
<tr>
<th>Wavelength/nm</th>
<th>Strength</th>
<th>MO Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>379.04</td>
<td>0.0508</td>
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<td>387.04</td>
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<td>HOMO-2 -&gt; LUMO</td>
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<td>395.70</td>
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<td>HOMO-1 -&gt; LUMO</td>
<td>95%</td>
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<td>406.77</td>
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<td>95%</td>
</tr>
<tr>
<td>478.47</td>
<td>0.0696</td>
<td>HOMO -&gt; LUMO+1</td>
<td>92%</td>
</tr>
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<td>759.29</td>
<td>0.5479</td>
<td>HOMO -&gt; LUMO</td>
<td>103%</td>
</tr>
</tbody>
</table>
$^1$H NMR spectrum of compound **10** (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 13 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 14 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 15 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 16 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 2o (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 18 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 19 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 20 (300 MHz, CDCl₃, TMS)
$^1$H NMR spectrum of compound 21 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 22 (300 MHz, CDCl$_3$, TMS)
$^1$H NMR spectrum of compound 3o (300 MHz, CDCl$_3$, TMS)
IR spectrum of compound 1o (ATR; diamond prism, neat)
IR spectrum of compound 13 (ATR; diamond prism, neat)
IR spectrum of compound 14 (ATR; diamond prism, neat)
IR spectrum of compound 15 (ATR; diamond prism, neat)
IR spectrum of compound 16 (ATR; diamond prism, neat)
IR spectrum of compound 2o (ATR; diamond prism, neat)
IR spectrum of compound 18 (ATR; diamond prism, neat)
IR spectrum of compound 19 (ATR; diamond prism, neat)
IR spectrum of compound 20 (ATR; diamond prism, neat)
IR spectrum of compound 21 (ATR; diamond prism, neat)
IR spectrum of compound 22 (ATR; diamond prism, neat)
IR spectrum of compound 3o (ATR; diamond prism, neat)
SI-7. Mass spectra

LRMS spectrum of compound 1o

File: YOK-BOO-3-174-1  
Sample: Description  
Instrument: JEOL MSRoute  
Inlet: Direct Probe  

Scan: 468  
Base: m/z 477; 27%FS  
TIC: 2344704

Date Run: 2009-11-27 (Time Run: 10:19:32)  
R.T.: 5.3  
Ionization mode: El+  

#Ions: 400
LRMS spectrum of compound 14

Scan: 63
Base: m/z 301; 67.2% FS TIC: 2782972

R.T.: 2.6

File: YOK-kose83-1
Sample: Description
Instrument: JEOL MSRoute
Inlet: Direct Probe

Date Run: 2010-01-12 (Time Run: 17:06:56)
Ionization mode: EI+

#Ions: 268
LRMS spectrum of compound 15

Scan: 62
Base: m/z 229; 65.7%FS TIC: 1830955

2010/01/12
Date Run: 2010-01-12 (Time Run: 17:14:27)
Ionization mode: EI+

R.T.: 2.55
#Ions: 167
LRMS spectrum of compound 16

Scan: 98
Base: m/z 432; 46.9%FS TIC: 2344603

Date Run: 2010-01-12 (Time Run: 17:20:58)
Ionization mode: EI+
R.T.: 4.07
#Ions: 503
LRMS spectrum of compound 2o

File: YOK-KOSE157-3-cry
Sample: Description
Instrument: JEOL MSRoute
Inlet: Direct Probe

Scan: 429
Base: m/z 537; 2.5%FS TIC: 210534

Date Run: 2009-11-27 (Time Run: 10:08:51)
Ionization mode: EI+
R.T.: 4.86
#Ions: 110
LRMS spectrum of compound 18

File: YOK-BOO-3-140-1
Sample: Description
Instrument: JEOL MSRoute
Inlet: Direct Probe

Date Run: 2009-12-15 (Time Run: 15:05:58)
Ionization mode: EI+

Scan: 30
Base: m/z 200; 2.1%FS TIC: 68654

R.T.: 1.23
#Ions: 22
LRMS spectrum of compound 19

Date Run: 2009-12-15 (Time Run: 15:52:46)
Ionization mode: EI+

R.T.: 2.8

Scan: 68
Base: m/z 278; 5.5%FS TIC: 311118

File: YOK-BOO-3-144-3
Sample: Description
Instrument: JEOL MSRoute
Inlet: Direct Probe

#Ions: 70
LRMS spectrum of compound 20

Scan: 59
Base: m/z 281; 14.1%FS TIC: 497482

Date Run: 2009-12-15 (Time Run: 15:30:19)
Ionization mode: EI+
R.T.: 2.43

#Ions: 98
LRMS spectrum of compound 21

Scan: 54
Base: m/z 224; 1.2%FS TIC: 43028

File: YOK-BOO-3-148-1
Sample: Description
Instrument: JEOL MSRoute
Inlet: Direct Probe

Date Run: 2009-12-15 (Time Run: 15:20:04)
Ionization mode: EI+

R.T.: 2.23

#Ions: 20
LRMS spectrum of compound 22

Date Run: 2009-10-13 (Time Run: 15:17:09)

Ionization mode: EI+

Scan: 367
Base: m/z 422; 13.2% FS TIC: 531353

R.T.: 4.15

#Ions: 205
LRMS spectrum of compound 3o

Date Run: 2009-11-27 (Time Run: 09:57:46)

Ionization mode: EI+

R.T.: 5.21

#Ions: 102

File: YOK-BOO-3-1160-1 2nd
Sample: Description
Instrument: JEOL MSRoute
Inlet: Direct Probe

Scan: 460
Base: m/z 91; 3.5%FS TIC: 278478