Electronic Supporting Infomation

4,4'-bithiazole-based tetraarylenes : new photochromes with unique photoreactive patterns

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General:

¹H NMR and ¹³C NMR are taken on either Bruker AM 360 (360 MHz), AM 300 (300 MHz) or AM (250 MHz) spectrometer and calibrated to the residual solvent peaks (CDCl₃, 7.24 ppm and 77 ppm). The data are reported as chemical shift (ppm). UV-Vis absorption spectra were recorded on a Varian Cary 5000 spectrometer equipped with a temperature control unit. An Oriel[®]Hg (Xe) 200 W lamp equipped with appropriate interference filters was used for sample irradiation. Solvents and reagents are used as received unless otherwise stated. Elemental analyses were performed by Service de Microanalyse, ICSN, 91198, Gif sur Yvette cedex, France.

<u>HPLC</u>: Analytic and semi-preparative HPLC of an irradiated (365 nm) **50** solution ($CH_2Cl_2/MeOH$:1/9) were performed using a Berger SFC MiniGram instrument and Princeton-2 ethylpyridine column.

<u>Quantum yield determination</u>: The photochromic reaction was induced by a continuous wavelength irradiation Hg/Xe lamp (Hamamatsu, 200 W) equipped with narrow band interference filters of appropriate wavelengths. The irradiation power was measured by a photodiode from Ophir (PD300-UV). The photochromic quantum yields were determined by probing the sample with a xenon lamp during the photochromic reaction. Absorption changes were monitored by a CCD camera mounted with a spectrometer (Princeton instruments). Kinetic profiles were analysed by an Igor implemented home-made software.

Syntheses and characterizations



Synthetic Scheme of 1o-5o

4,4'-di(2-phenyl)thiazole



1,4-dibromobutane-2,3-dione (1.22 g, 5 mmol) was added in one portion to a solution of thiobenzamide (1.37 g, 10 mmol) in MeOH (ca. 30 ml) and the mixture was then refluxed overnight and allowed to cool down to room temperature. The precipitate was filtered, washed with MeOH and vacuum dried to furnish 4,4'-di(2-phenyl)dithiazole as a off-white crystalline solid (1.40 g, 87%). The product was pure enough for next step.

¹H NMR (CDCl₃, 360 MHz) : δ = 7.44 (m, 6 H), 7.94 (s, 2H), 8.03 (dd, 4H).

2,2'-dibromo-di(2-phenyl)thiazole



Bromine (1.1 ml, 21 mmol) was added in one portion to 4,4'-di(2-phenyl)dithiazole (1.60 g, 5 mmol) in MeCN (25 ml) and CHCl₃ (25 ml) and the mixture was stirred ca. 20 min at room temperature, then refluxed overnight. The mixture was cooled to room temperature and exces of bromine was reduced by treating the mixture with an aqueous solution of $Na_2S_2O_5$. Then, organic solvents were removed by rotary evaporator and almost colorless precipitate filtered

and washed with water. The wet precipitate was dissolved in CH_2Cl_2 (ca. 30 ml) then MeOH (ca. 30 ml) was added. CH_2Cl_2 removal of the solution by rotary evaporator led to the precipitation of the compound, which was filtered, washed with MeOH and vacuum dried. The compound was obtained as an off-white and crystalline solid (2.08 g, 87%).

Alternative method: NBS (1.60 g, 9 mmol) was added portion wise to 4,4'-di(2-phenyl)dithiazole (1.28 g, 4 mmol) dissolved in DMF (20 ml) at ca. 70 °C and a lightly colored precipitate formed quickly. After ca. 1-2 h at this temperature, H_2O (ca. 60 ml) followed by $Na_2S_2O_5$ (ca. 0.4 g) were introduced at room temperature. After stirring the mixture for ca. 0.5 h, the precipitate was filtered, washed with H_2O and vacuum dried (1.83 g, 96%). The compound was pure enough for next step.

¹H NMR (CDCl₃, 360 MHz) : δ = 7.44 (m, 6 H), 7.93 (dd, 4H).

Elemental analysis calcd (%) for $C_{18}H_{10}Br_2N_2S_2$: C 45.21, H, 2.11, N 5.86 ; found : C 45.31, H, 2.03, N 5.86.

4-Bpin-5-Me-2-phenylthiazole (6)



a) 4-Br-5-Me-2-phenylthiazole¹



4-Br-5-Me-2-phenylthiazole was most conveniently synthesized using reported Halogen-Dance reaction of thiazole.² Thus, LDA (2 M, 1.5 ml) was added dropwise into a solution of 5-Br-2-phenylthiazole² (480 mg, 2 mmol) in dry THF (20 ml) at -78 °C. After stirring 10 to 15 min. at that temperature, iodomethane (0.2 ml, 3.2 mmol) was introduced and the solution was kept at that temperature for ca. 1-2 h before slowly warming up to room temperature. After quenching the mixture with aqueous NH₄Cl solution (2 M, 20 ml), ether (ca. 20 ml) was added. After separation of the organic phase, aqueous phase was then extracted twice with diethyl ether (20 ml). Combined organic phase was washed with brine (30 ml) and dried over Na₂SO₄. After removal of solvents, column chromatography (SiO₂, CH₂Cl₂) of the residue gave 4-Br-5-Me-2-phenylthiazole as a white crystalline solid (460 mg, 91%).

¹H NMR (CDCl₃, 360 MHz) : δ = 7.85 (m, 2H), 7.39 (m, 3H), 2.41 (s, 3H).

b) 4-Bpin-5-Me-2-phenylthiazole was synthesized as described in the literature.³

4-Bpin-5-Me-2-(2'-pyridyl)thiazole (7)



Under argon nBuLi (3.2 ml, 1.6 M) was added dropwise to 4-Br-5-Me-2-(2'-pyridyl)thiazole⁴ (1.147 g, 4.5 mmol) in 30 ml dry ether at -78 °C. The mixture was stirred at that temperature for ca. 1 h and then iPrOBpin (2-isopropoxy-4,4,5,5-tetramethyl-1.3.2-dioxaborolane, 1.4 ml, 6.7 mmol) was introduced. The mixture was allowed to slowly warm to room temperature and aqueous NH₄Cl (25 ml, ca. 2 M) was added. After few min., the aqueous phase was further

extracted twice with diethyl ether (20 ml). The combined organic phase was washed with brine (30 ml) and dried over Na_2SO_4 . After removal of the solvent, the oil residue cristallized rapidly to give a light brown solid (1.220 g, 90%). The boronic ester was used in next step without further purification.

¹H NMR (CDCl₃, 300 MHz) : $\delta = 8.53$ (d, 1H), 8.28 (d, 1H), 7.71 (t, 1H), 7.21 (t, 1H), 2.73 (s, 3H), 1.37 (s, 12H).

4-Bpin-5-Me-2-phenyloxazole (8)



a) Starting with 5-Br-2-phenyloxazole,⁵ Br-5-Me-2-phenyloxazole was prepared in the same way as 4-Br-5-Me-2-phenylthiazole by Halogen-Dance reaction in 97% as a white and crystalline solid.

¹H NMR (CDCl₃, 300 MHz) : δ = 7.96 (m, 2H), 7.42 (m, 3H), 2.37 (s, 3H).

b) 8 was prepared similarly as 6 in 89% as a white solid and used without further purification.

¹H NMR (CDCl₃, 300 MHz) : δ = 8.06 (m, 2H), 7.38 (m, 3H), 2.54 (s, 3H), 1.34 (s, 12H).

4-B(OH)₂-2-Me-5-phenylthiophene (9)



9 was prepared according to literature procedure.⁶

Tetraarylene 10



2,2'-dibromo-di(2-phenyl)thiazole (120 mg, 0.25 mmol), **6** (180 mg, 0.60 mmol), CsF (210 mg, 1.38 mmol) and Pd(PPh₃)₄ (22 mg, 0.019 mmol) were purged three times by alternating vacuum and Ar. Then, similarily purged dioxane (15 ml) was introduced and the mixture was refluxed under Ar overnight. At room temperature, CHCl₃ (ca. 20 ml) followed by H₂O (20 ml) were added and stirred vigorously for few min.. Then, the organic phase was separated and the aqueous phase was extracted twice with CHCl₃ (ca. 10 ml). The combined organic phase was washed with brine (30 ml) and dried over Na₂SO₄. **10** was obtained after column chromatography (SiO₂, CH₂Cl₂) as an off-white crystalline solid (110 mg, 66%).

Single crystals suitable for X-ray structure determination were obtained by slow evaporation of 10 in a mixture of MeOH and a minimum amount of CH_2Cl_2 .

MP : 230-231 °C (uncorrected).

¹H NMR (CDCl₃, 250 MHz) : $\delta = 8.08$ (m, 4H), 7.45 (m, 10H), 7.12-7.27 (m, 6H), 2.01 (s, 6H).

¹³C NMR (CDCl₃, 63 MHz) : δ = 168.3, 164.3, 147.6, 142.6, 133.7, 133.3, 132.5, 130.8, 130.5, 129.4, 129.1, 128.6, 127.0, 126.1, 12.3.

ESI-HRMS (m/z) [MH]⁺: calcd: 667.1119 ; found: 667.1090.

Elemental analysis calcd (%) for $C_{38}H_{26}N_4S_4$: C 68.44, H 3.93, N 8.40; found : C 68.53, H 3.93, N 8.40.

Tetraarylene 20



20 was synthesized in a similar way to **10** except the use of **7** instead of **6**, and was obtained, after column chromatography (SiO₂, CH₂Cl₂ to 5% Et₂O), as a white crystalline solid in a yield of 83%.

Single crystals suitable for X-ray structure determination were obtained by slow evaporation of 20 in a mixture of MeOH and a minimum of CH_2Cl_2 .

MP: 278-279 °C (uncorrected).

¹H NMR (CDCl₃, 360 MHz) δ = 8.15 (d, 2H), 8.06 (m, 4H), 7.89 (d, 2H), 7.62 (t, 2H), 7.45 (m, 6H), 7.08 (dd, 2H), 2.06 (s, 6H).

¹³C NMR (CDCl₃, 90 MHz) : δ =168.3, 165.1, 151.0, 148.9, 147.9, 136.7, 136.6, 135.4, 133.7, 133.6, 130.5, 129.1, 127.0, 123.7, 119.6, 12.4.

ESI-HRMS (m/z) [MH]⁺: calcd: 669.1024; found: 669.1018.

Elemental analysis calcd (%) for $C_{38}H_{24}N_6S_{4.0.15}CH_2Cl_2$: C 63.76, H 3.99, N 11.65; found : C 63.63, H 3.36, N 12.26.

Tetraarylene 3o



30 was synthesized in a similar way to **10** except the use of **8** instead of **6**, and was obtained, after column chromatography (SiO₂, CH₂Cl₂), as an off-white crystalline solid in a yield of 75%.

MP: 191-192 °C (uncorrected).

¹H NMR (CDCl₃, 250 MHz) : $\delta = 8.06$ (m, 4H), 7.60 (d, 4H), 7.45 (m, 6H), 7.10 (m, 6H), 1.97 (s, 6H).

¹³C NMR (CDCl₃, 63 MHz) : δ = 168.5, 160.3, 146.6, 137.4, 133.6, 130.5, 129.8, 129.1, 128.7, 128.4, 128.0, 126.9, 126.6, 126.1, 10.9.

ESI-HRMS (m/z) [MH]⁺: 635.1575 ; found : 635.1570.

Elemental analysis calcd (%) for $C_{38}H_{24}N_4O_2S_2$: C 71.90, H 4.13, N 8.83; found : C 71.50, H 4.19, N 8.56.

Tetraarylene 40



40 was synthesized in a similar way to **10** except the use of **9** instead of **6**, and was obtained, after column chromatography (SiO₂, CH₂Cl₂), as a yellow crystalline solid in a yield of 72%. MP : 149-150 °C (uncorrected).

¹H NMR (CDCl₃, 250 MHz) : $\delta = 8,04$ (m, 4H), 7.45 (m, 6H), 7.15-7.29 (m, 10H), 6.68 (s, 2H), 2.06 (s, 6H).

¹³C NMR (CDCl₃, 63 MHz) : δ =167.7, 147.1, 140.4, 137.2, 133.9, 133.7, 131.2, 130.4, 129.1, 128.9, 128.8, 127.3, 126.9, 125.4, 125.1, 14.3.

ESI-HRMS (m/z) [MH]⁺: calcd: 665.1214; found: 665.1204.

Elemental analysis calcd (%) for $C_{40}H_{28}N_2S_4$: C 72.25, H 4.24, N 4.21; found : C 72.37, H 4.28, N 4.15.

Tetraarylene 50



50 was prepared in a similar way as **10** except that two boronic esters (1.05 eq. of **7** and 1.05 eq. of **8** relative to that of 2,2'-dibromo-di(2-phenyl)thiazole) were used simultaneously. **50** was obtained, after column chromatography (SiO₂, CH₂Cl₂ to 4% Et₂O), as an off-white crystalline solid in a yield of 31%.

Single crystals suitable for X-ray structure determination were obtained by slow evaporation of **50** in a mixture of tBuOMe and a minimum of CH_2Cl_2 .

MP: 218-219 °C (uncorrected).

¹H NMR (CDCl₃, 360 MHz) : δ = 8.21 (d, 1H), 8.08 (m, 2H), 8.04 (m, 2H), 7.81 (d, 1H), 7.58 (d, 2H), 7.45 (m, 7H), 7.15 (m, 3H), 7.02 (dd, 1H), 2.05 (s, 3H), 2.01 (s, 3H).

¹³C NMR (CDCl₃, 90 MHz) : $\delta = 168.7$, 168.5, 159.8, 150.8, 149.1, 147.8, 146.8, 146.7, 143.1, 136.6, 135.4, 133.6, 130.6, 130.5, 130.3, 129.7, 129.1, 128.4, 128.2, 128.1, 127.0, 126.9, 126.0, 119.3, 12.4, 10.9.

ESI-HRMS (m/z) [MH]⁺: calcd : 652.1299 ; found: 652.1281.

Elemental analysis calcd (%) for $C_{37}H_{25}N_5OS_3$: C 68.18, H 3.87, N 10.74 ; found C 68.01, H 3.93, N 10.71.

References:

- 1) K. Uchida, T. Ishikawa, M. Takeshita, M. Irie, *Tetrahedron*, 1998, 54, 6627.
- 2) T. Nakashima, K. Atsumi, S. Kawai, T. Nakagawa, Y. Hasegawa, T. Kawai, *Eur. J. Org. Chem.*, 2007, 3212.
- 3) J. Hämmerle, M. Shnürch, N. Iqbal, M. D. Mihovilovic, P. Stanetty, *Tetrahedron*, 2010, 66, 8051.
- 4) M. Giraud, A. Léaustic, M. F. Charlot, P. Yu, M. Césario, C. Philouze, R. Pansu, K. Nakatani, E. Ishow, *New J. Chem.*, 2005, **29**, 439.
- 5) E. Vedejs, S. D. Monahan, J. Org. Chem., 1997, 62, 4763.
- 6) J. Kühni, V. Adamo, P. Belser, Synthesis, 2006, 1946.

Fig. S1 : Chromatogram of analytic HPLC of a UV (365 nm) irradiated solution of **50** (CH₂Cl₂/MeOH: 1/9) with retention time of 1.4 min for **50**, 2.5 min for **5c**₁ and 2.8 min for **5c**₂.



Fig. S1bis : Chromatogram of semi-preparative HPLC of a UV (365 nm) irradiated solution of 50 (CH₂Cl₂/MeOH: 1/9) :



Three injections were necessary to get enough solution of each closed form $5c_1$ and $5c_2$ for UV-Vis spectra recording.

UV-Vis data :



Fig. S2: Absorption spectra of **20** and its photostationary state (320 nm) in MeCN solution (c : $2.90 \ 10^{-5} \text{ M}$) at room temperature.



Fig. S3: Absorption spectra of **30** and its photostationary state (320 nm) in MeCN solution (c : $3.10 \ 10^{-5} \text{ M}$) at room temperature.



Fig. S4: Absorption spectra of **40** and its photostationary state (320 nm) in MeCN solution (c : $2.10 \ 10^{-5} \text{ M}$) at room temperature.



Fig. S5: Absorption spectra of **50** and its photostationary state (320 nm) in MeCN solution (c : $2.40 \ 10^{-5} \text{ M}$) at room temperature.



Fig. S5bis: Absorption spectra of 50, $5c_1$, $5c_2$ and its photostationary state (320 nm) as well as its convoluted spectrum (MeCN, room temperature). The convoluted spectrum was obtained by the combination of the three spectra of 50, $5c_1$ and $5c_2$ with coefficients corresponding to their concentrations at photostationary state.



Fig. S6: Aliphatic portions of ¹H NMR spectra in $CDCl_3$ at room temperature of **50** before (red) and upon UV irradiation at 365 nm (blue), and also those of UV irradiated (365 nm) **20** (green) and **30** (violet) in $CDCl_3$ included for comparison.



Fig. S7: Concentration profiles of the three components $(50, 5c_1 \text{ and } 5c_2)$ as a function of irradiation time at different excitation wavelength.

X-ray crystallography:

X-ray diffraction data for **10**, **20** and **50** were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo_{Ka} radiation ($\lambda = 0.71073$ Å). Crystals of **10** and **50** were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100K) by means of a 700 series Cryostream cooling device within an accuracy of ±1 K. For **20** recording was performed at room temperature. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97ⁱ and refined against F^2 by full-matrix least-squares techniques using SHELXL-97ⁱⁱ with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.ⁱⁱⁱ

The crystal data collection and refinement parameters are given in Table 1.

CCDC 889067, 889068 and 889294 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

ⁱ Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.

ⁱⁱ Sheldrick, G. M. SHELXL-97, Program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany, **1997**.

ⁱⁱⁱ Farrugia, L. J. J. Appl. Cryst., **1999**, 32, 837-838.

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Fig. S8 : ORTEP view (10% probability thermal ellipsoids) of **10**.



Fig. S9: ORTEP view (10% probability thermal ellipsoids) of **20**.



Fig. S10 : ORTEP view (10% probability thermal ellipsoids) of 50

Compound	10	20	50
Formula	$C_{38}H_{26}N_4S_4$	$C_{36}H_{24}N_6S_4$	$C_{37}H_{25}N_5OS_3$
M _r	666.87	668.89	651.83
Crystal size, mm ³	0.31 x 0.27 x 0.21	0.32 x 0.28 x 0.25	0.31 x 0.28 x 0.04
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_l/n$	C 2/c	P -1
a, Å	11.9309(6)	19.3210(17)	9.7383(15)
b, Å	13.5973(7)	9.8395(8)	11.8198(17)
c, Å	19.9102(9)	17.5549(16)	15.4915(19)
α, °	90	90	93.571(3)
β, °	95.9330(10)	107.090(2)	106.219(3)
γ, °	90	90	112.544(3)
Cell volume, Å ³	3212.7(3)	3190.0(5)	1552.2(4)
Z	2	4	2
Т, К	100(1)	293(2)	100(1)
F ₀₀₀	1384	1384	676
μ , mm ⁻¹	0.331	0.335	0.279
θ range, °	1.91 - 36.72	2.21 - 38.45	1.90 - 32.95
Reflection collected	57 823	29 991	25 096
Reflections unique	15 517	8 474	10 546
R _{int}	0.0319	0.0284	0.0690
GOF	1.024	1.022	1.054
Refl. obs. $(I \ge 2\sigma(I))$	11 572	4 597	5 644
Parameters	417	209	417
wR ₂ (all data)	0.1113	0.1874	0.2448
R value $(I \ge 2\sigma(I))$	0.0406	0.0592	0.0783
Largest diff. peak and hole (eÅ ⁻³)	-0.373 ; 0.670	-0.334 ; 0.493	-0.329 ; 0.459