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The synthesis of polyarene-modified 5-phenyl-2,2'-bipyridines *via* the S_N^H methodology and aza-Diels−Alder reaction

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General. All common reagents and solvents were used as purchased. Melting points were measured on the instrument Boetius. NMR spectra were acquired on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, using TMS as internal standard. Mass-spectra were recorded on MicrOTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyzes (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer.

6-Phenyl-3-(2-pyridyl)-1,2,4-triazine **1**,[1] 1-bromopyrene **2a**,[2] 9-bromophenanthrene **2b**[3] were synthesized according to literature methods.

2-Bromotriphenylene (2c). Synthesis was performed by an improved method.[4] Triphenylene **3c** (2 g, 8.76 mmol) was dissolved in dichloromethane (30 ml). Bromine (0.5 ml, 9.64 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 1 week. Reaction mixture was washed with water sodium dithionite solution and with water, dried with anhydrous sodium sulfate. Dichloromethane was removed under the reduced pressure. The product was used in the next step without addition purification. Yield 2.15 g (7 mmol, 80%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.63-7.70 (m, 4H), 7.73 (dd, 1H, ^3J 8.8 Hz, ^4J 2.0 Hz, H-3), 8.48 (d, 1H, ^3J 8.8 Hz, H-4), 8.53-8.59 (m, 2H), 8.61-8.68 (m, 2H), 8.75 (d, 1H, ^4J 2.0 Hz, H-1).

General method for the synthesis of σ-adducts **4**

Corresponding bromosubstituted polynuclear arene **2** (2.19 mmol) was dissolved in dry THF (20 ml) in a Schlenk flask under argon atmosphere and cooled to -78 ºC. *sec*-BuLi solution in hexane (1.3 M, 1.85 ml) was added and the resulting mixture was stirred at -78 ºC for 5 min. Solution of 1,2,4-triazine **1** (0.41 g, 1.75 mmol) in dry toluene (20 ml) was then added and the resulting mixture was stirred overnight at room temperature. The reaction mixture was washed

with water and dried with anhydrous sodium sulfate. Solvents were removed under the reduced pressure. The products were isolated by column chromatography (eluent: hexane, then ethylacetate). All the compounds obtained were transferred for the next step without the additional purification.

6-Phenyl-5-(pyren-1-yl)-3-(2-pyridyl)-4,5-dihydro-1,2,4-triazine (4a). Yield 730 mg (1.68 mmol, 96%). Mp 117-119 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.00 (s, 1H, H(C-sp^3)), 7.26-7.33 (m, 4H, Ph, H-5 (py)), 7.62 (ddd, 1H, ^3J 7.8, 7.8 Hz, ^4J 1.6 Hz, H-4 (py)), 7.75 (m, 2H, Ph), 7.86 (d, ^3J 8.0 Hz, pyrene), 7.96-8.05 (m, 4H, pyrene), 8.09 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.17 (d, ^3J 7.6 Hz, pyrene), 8.25 (d, ^3J 7.6 Hz, pyrene), 8.31 (d, 1H, ^3J 9.6 Hz, H-3 (pyrene)), 8.50 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)), 9.15 (d, 1H, ^3J 9.6 Hz, H-2 (pyrene)), 10.28 (s, 1H, NH). **^{13}C NMR** ($CDCl_3$, δ, ppm): 54.9 (C-sp^3), 121.4, 124.5, 124.9, 125.0, 125.1, 125.2, 125.3, 125.4, 125.7, 126.0, 126.6, 127.4, 127.5, 128.0, 128.5, 129.1, 129.5, 130.9, 131.2, 131.3, 132.3, 135.0, 136.8, 143.4, 148.0, 149.4, 149.5. **ESI-MS**, *m/z*: found 437.18, calculated 437.18 $(M+H)^+$.

5-(Phenanthren-9-yl)-6-phenyl-3-(2-pyridyl)-4,5-dihydro-1,2,4-triazine (4b). Yield 680 mg (1.66 mmol, 95%). Mp 104-106 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 6.75 (s, 1H, H(C-sp^3)), 7.27-7.36 (m, 4H, Ph, H-5 (py)), 7.50 (м, 1H, phenanthrene), 7.54 (s, 1H, H-10 (phenanthrene)), 7.59 (m, 1H, phenanthrene), 7.66 (ddd, 1H, ^3J 7.8, 7.8 Hz, ^4J 1.6 Hz, H-4 (py)), 7.70-7.85 (m, 5H, Ph, phenanthrene), 8.08 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.51 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)), 8.64 (m, 1H, phenanthrene), 8.76 (m, 1H, phenanthrene), 9.05 (m, 1H, phenanthrene), 10.28 (s, 1H, NH). **^{13}C NMR** ($CDCl_3$, δ, ppm): 55.1 (C-sp^3), 121.4, 122.4, 123.1, 125.4, 125.8, 126.2, 126.4, 126.6, 126.6, 126.7, 126.8, 128.5, 129.1, 129.6, 130.4, 130.5, 131.4, 131.5, 131.5, 134.9, 136.9, 142.8, 148.0, 149.5, 149.7. **ESI-MS**, *m/z*: found 413.18, calculated 413.18 $(M+H)^+$.

6-Phenyl-3-(2-pyridyl)-5-(triphenylen-2-yl)-4,5-dihydro-1,2,4-triazine (4c). Yield 770 mg (1.66 mmol, 95%). Mp 147-149 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 6.22 (s, 1H, H(C-sp^3)), 7.37 (m, 4H, Ph, H-5 (py)), 7.62 (m, 4H, Ph, triphenylene), 7.71-7.82 (m, 2H, H-4 (py), H-3 (triphenylene)), 7.85 (m, 2H, triphenylene), 8.25 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.54-8.64 (m, 6H, H-6 (py), triphenylene), 8.73 (d, 1H, ^4J 1.2 Hz, H-1 (triphenylene)), 10.32 (s, 1H, NH). **^{13}C NMR** ($CDCl_3$, δ, ppm): 57.7 (C-sp^3), 121.3, 122.3, 123.2, 123.2, 123.3, 123.5, 124.1, 125.6, 126.7, 126.8, 127.2, 127.3, 128.6, 129.4, 129.5, 129.6, 129.7, 129.8, 129.8, 129.9, 130.2, 135.1, 137.1, 139.0, 143.9, 148.2, 149.5, 149.8. **ESI-MS**, *m/z*: found 463.19, calculated 463.19 $(M+H)^+$.

General procedure for the synthesis of triazines **5**

The corresponding adducts **4** (1 mmol) were dissolved in dichloromethane (25 ml). DDQ (250 mg, 1.1 mmol) was added at once and the reaction mixture was stirred at room temperature for 30 min. Solvent was removed under the reduced pressure. The oily residue was purified by the column chromatography (neutral Al_2O_3, eluent – ethylacetate). The pure analytical samples were obtained by the recrystallization from acetonitrile.

6-Phenyl-5-(pyren-1-yl)-3-(2-pyridyl)-1,2,4-triazine (5a). Yield 390 mg (0.91 mmol, 91%). Mp 196-198 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.10 (m, 2H, Ph), 7.18 (m, 1H, Ph), 7.50 (m, 3H, Ph, H-5 (py)), 7.92-8.11 (m, 6H, H-4 (py), pyrene), 8.12-8.20 (m, 3H, pyrene), 8.24 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.78 (d, 1H, ^3J 8.0 Hz, H-2 (pyrene)), 8.91 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 123.7, 124.3, 124.4, 124.7, 124.8, 125.6, 125.9, 126.0, 126.4, 127.3, 127.9, 128.4, 128.6, 128.9, 128.9, 129.3, 129.7, 130.3, 130.7, 131.2, 132.5, 134.8, 137.3, 150.3, 152.7, 157.8, 158.2, 160.7. **ESI-MS**, *m/z*: found 435.16, calculated 435.16 $(M+H)^+$. Found, %: C 82.77, H 3.97, N 12.67. **$C_{30}H_{18}N_4$**. Calculated, %: C 82.93, H 4.18, N 12.89.

5-(Phenanthren-9-yl)-6-phenyl-3-(2-pyridyl)-1,2,4-triazine (5b). Yield 340 mg (0.83 mmol, 83%). Mp 219-221 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.14 (m, 2H, phenanthrene), 7.21 (m, 1H, phenanthrene), 7.42 (m, 1H, phenanthrene), 7.50 (m, 1H, H-5 (py)), 7.57-7.66 (m, 5H, Ph), 7.73 (m, 1H, phenanthrene), 7.87 (m, 1H, phenanthrene), 7.91-7.98 (m, 2H, H-10 (phenanthrene), H-4 (Py)), 8.71 (m, 2H, phenanthrene), 8.77 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.93 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 122.7, 123.1, 124.3, 125.5, 125.8, 127.0, 127.1, 128.0, 128..4, 128.9, 129.0, 129.3, 129.4, 129.8, 130.4, 130.5, 130.8, 131.0, 132.8, 134.7, 137.1, 150.6, 152.8, 157.5, 157.9, 161.1. **ESI-MS**, *m/z*: found 411.16, calculated 411.16 $(M+H)^+$. Found, %: C 81.71, H 4.26, N 13.54. **$C_{28}H_{18}N_4$**. Calculated, %: C 81.93, H 4.42, N 13.65.

6-Phenyl-3-(2-pyridyl)-5-(triphenylen-2-yl)-1,2,4-triazine (4c). Yield 370 mg (0.81 mmol, 81%). Mp 171-173 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.36-7.49 (m, 3H, Ph), 7.52 (m, 1H, H-5 (py)), 7.60 (m, 1H, triphenylene), 7.63-7.77 (m, 5H, Ph, triphenylene, H-4 (py)), 7.97 (m, 2H, triphenylene), 8.29 (dd, 1H, ^3J 8.0 Hz, ^4J 1.6 Hz, H-3 (py)), 8.57-8.69 (m, 4H, triphenylene), 8.79 (d, 1H, ^3J = 8.0 Hz, H-4 (triphenylene)), 8.96 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)), 9.02 (d, 1H, ^4J 1.2 Hz, H-1 (triphenylene)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 123.3, 123.4, 123.6, 123.8, 124.0, 124.3, 125.5, 125.9, 127.5, 127.7, 128.0, 128.2, 128.9, 129.0, 129.3, 129.6, 129.7, 129.8, 129.9, 130.5, 131.6, 133.8, 134.4, 135.7, 137.2, 150.5, 153.0, 156.1, 156.8, 160.9. **ESI-MS**, *m/z*: found 461.17, calculated 461.18 $(M+H)^+$. Found, %: C 83.33, H 4.14, N 11.93. **$C_{32}H_{20}N_4$**. Calculated, %: C 83.46, H 4.38, N 12.17.

General procedure for the synthesis of bipyridines **6a-c**

Corresponding 1,2,4-triazines **5** (0.8 mmol) were suspended in *o*-xylene (25 ml). 2,5-Norbornadiene (0.4 ml, 4 mmol) was added and the resulting mixture was stirred under reflux for 18 h while adding of 2,5-norbornadiene (0.4 ml, 4 mmol) for every 6 h. Solvent was removed under the reduced pressure, and the residue was purified by the column chromatography (silica gel, eluent – ethylacetate). The pure products were obtained by the recrystallization from acetonitrile.

5-Phenyl-6-(pyren-1-yl)-2,2'-bipyridine (6a). Yield 270 mg (0.63 mmol, 79%). Mp 214-216 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.02 (m, 3H, Ph), 7.09-7.14 (m, 2H, Ph), 7.31 (m, 1H, H-5 (py)), 7.75 (ddd, 1H, ^3J 7.8, 7.8 Hz, ^4J 1.6 Hz, H-4 (py)), 7.82 (d, 1H, ^3J 8.0 Hz, H-3 (pyrene)), 7.96-8.10 (m, 6H, H-3 (py, center), pyrene), 8.12-8.17 (m, 2H, pyrene), 8.19 (d, ^3J 7.8 Hz, H-4 (py, center)), 8.49 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.62 (d, 1H, ^3J 8.0 Hz, H-2 (pyrene)), 8.74 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 119.7, 121.7, 123.8, 124.4, 124.8, 125.0, 125.2, 125.5, 125.9, 127.1, 127.4, 127.5, 127.6, 128.1, 128.5, 129.3, 129.4, 131.0, 131.1, 131.3, 135.8, 136.9, 138.1, 139.2, 139.3, 139.4, 149.2, 154.6, 156.1, 156.8. **ESI-MS**, *m/z*: found 433.17, calculated 433.17 $(M+H)^+$. Found, %: C 88.58, H 4.41, N 6.27. **$C_{32}H_{20}N_2$**. Calculated, %: C 88.86, H 4.66, N 6.48.

6-(Phenanthren-9-yl)-5-phenyl-2,2'-bipyridine (6b). Yield 260 mg (0.65 mmol, 81%). Mp 237-239 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.05 (m, 3H, Ph), 7.19 (m, 2H, Ph), 7.30 (m, 1H, H-5 (Py)), 7.47 (m, 1H, phenanthrene), 7.54 (m, 1H, phenanthrene), 7.58-7.67 (m, 3H, phenanthrene), 7.73 (m, 2H, phenanthrene, H-4 (Py)), 7.83 (m, 1H, phenanthrene), 8.03 (d, ^3J 8.0 Hz, H-3 (py, center)), 8.45 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.59 (d, 1H, ^3J 8.0 Hz, H-4 (py, center)), 8.66-8.75 (m, 3H, phenanthrene, H-6 (Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 119.9, 121.7, 122.5, 122.8, 123.8, 126.3, 126.5, 126.6, 126.8, 127.0, 127.2, 128.0, 128.1, 128.9, 129.3, 130.3, 130.6, 131.2, 131.3, 136.9, 137.1, 137.9, 139.2, 139.3, 149.1, 154.6, 156.1, 156.4. **ESI-MS**, *m/z*: found 409.17, calculated 409.17 $(M+H)^+$. Found, %: C 88.01, H 4.76, N 6.65. **$C_{30}H_{20}N_2$**. Calculated, %: C 88.21, H 4.93, N 6.86.

5-Phenyl-6-(triphenylen-2-yl)-2,2'-bipyridine (6c). Yield 270 mg (0.59 mmol, 77%). Mp 202-204 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.28-7.39 (m, 5H, Ph), 7.51-7.74 (m, 5H, H-5 (py), triphenylene), 7.83 (dd, 1H, ^3J 8.0 Hz, ^4J 1.2 Hz, H-3 (triphenylene)), 7.88 (ddd, 1H, ^3J 7.8, 7.8 Hz, ^4J 1.6 Hz, H-4 (py)), 7.96 (d, 1H, ^3J 8.0 Hz, H-3 (py, center)), 8.29 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.54 (m, 2H, H-4 (py, center), triphenylene), 8.60-8.68 (m, 3H, triphenylene), 8.70 (d, 1H, ^3J 8.0 Hz, H-4 (triphenylene)), 8.75 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)), 8.82 (d, 1H, ^4J 1.2 Hz, H-1 (triphenylene)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 119.4, 121.5, 122.9, 123.2, 123.3, 123.4, 123.5, 123.8, 125.7, 127.1, 127.2, 127.2, 127.3, 127.4, 128.6, 129.0, 129.3, 129.6,

129.8, 130.0, 130.1, 130.9, 132.5, 136.4, 136.9, 138.8, 139.8, 140.2, 149.2, 154.9, 155.8, 156.1. **ESI-MS**, *m/z*: found 459.19, calculated 459.19 $(M+H)^+$. Found, %: C 88.89, H 4.64, N 5.97. $\mathbf{C_{34}H_{22}N_2}$. Calculated, %: C 89.06, H 4.84, N 6.11.

4-Phenyl-3-(pyren-1-yl)-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenteno[*c*]pyridine (6d). 1,2,4-Triazine **5a** (300 mg, 0.69 mmol) was suspended in *o*-xylene (20 ml). 1-Morpholinocyclopentene (0.22 ml, 1.38 mmol) was added and the resulting mixture was stirred under reflux for 5 h. Then the additional portion of 1-morpholinocyclopentene (0.11 ml, 0.69 mmol) was added and the resulting mixture was stirred under reflux for 5 h. Solvent was removed under the reduced pressure. The desired product was isolated by recrystallization (acetonitrile). Yield 240 mg (0.52 mmol, 75%). Mp 205-207 ºC. **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.19 (m, 2H, 6-CH_2), 2.97 (t, 2H, ^3J 7.6 Hz, 7-CH_2), 3.64 (t, 2H, ^3J 7.6 Hz, 5-CH_2), 6.97-7.03 (m, 3H, Ph), 7.04-7.10 (m, 2H, Ph), 7.24 (m, 1H, H-5 (py)), 7.69-7.77 (m, 2H, H-4 (py)), H-3 (pyrene)), 7.95-8.05 (m, 5H, pyrene), 8.12-8.18 (m, 3H, pyrene), 8.31 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz, H-3 (py)), 8.72 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6 (py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 25.5, 33.1, 33.8, 122.7, 123.5, 124.1, 124.8, 124.9, 125.0, 125.8, 126.7, 126.8, 127.2, 127.3, 127.5, 127.8, 128.5, 129.5, 129.7, 130.6, 131.0, 131.3, 134.7, 136.2, 136.5, 138.1, 138.3, 146.3, 148.5, 150.3, 155.0, 155.6, 158.5. **ESI-MS**, *m/z*: found 473.20, calculated 473.20 $(M+H)^+$. Found, %: C 88.78, H 4.95, N 5.69. $\mathbf{C_{35}H_{24}N_2}$. Calculated, %: C 88.95, H 5.12, N 5.93.

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