ESI to accompany

# Factors controlling the photoresponse of copper(I) diimine dyes containing hole-transporting dendrons in dye-sensitized solar cells: substituent and solvent effects

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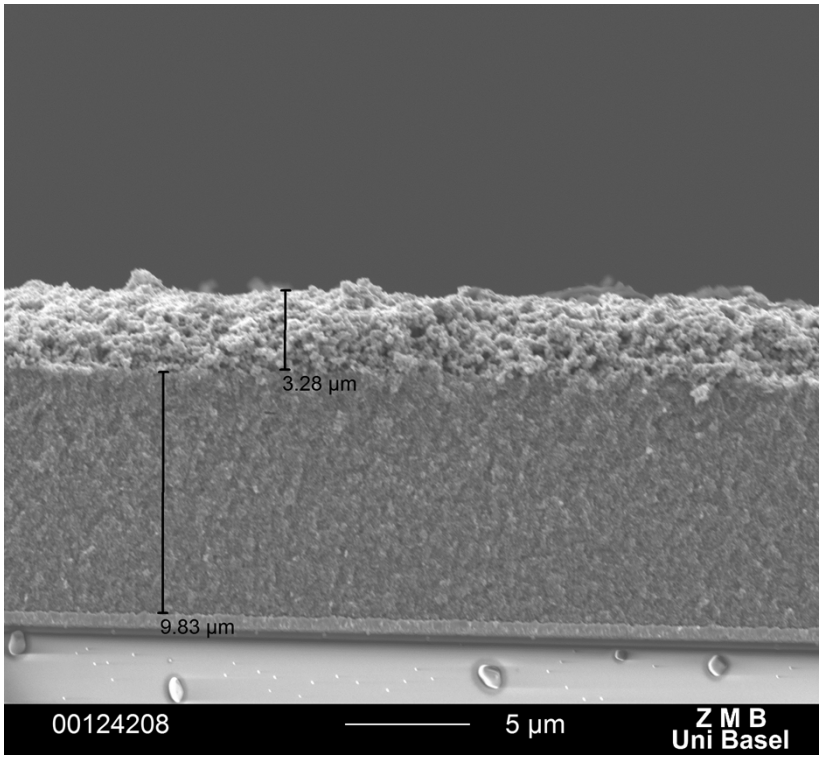



Fig. S1. Cross-section SEM micrograph of a commercial Solaronix electrode. Uniform and densely packed scattering and transparent layers with thicknesses of ~9 and 3 µm are observed, respectively.

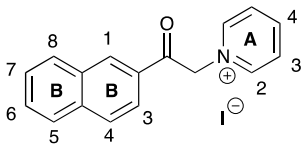
## Experimental Section for ligand synthesis

### General

Bis(4-methoxyphenyl)amine was purchased from Sigma-Aldrich and was used as received. 4,4'-Bis(4-bromophenyl)-6,6'-dimethyl-2,2'-bipyridine,[1] 4,4'-bis(N,N-

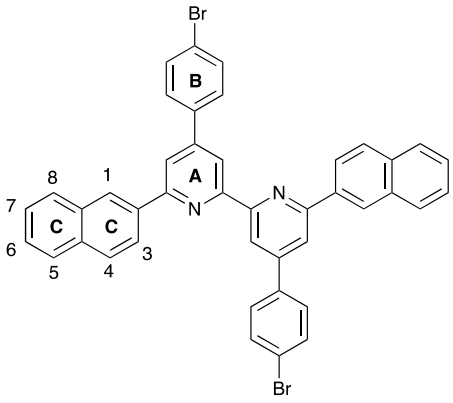
bis(4-methoxyphenyl)amino)diphenylamine,[1] 4,4'-bis(4-bromophenyl)-6,6'-di-*n*-butyl-2,2'-bipyridine,[2] 4,4'-bis(4-bromophenyl)-6,6'-diisobutyl-2,2'-bipyridine,[2] 4,4'-bis(4-bromophenyl)-6,6'-di-*n*-hexyl-2,2'-bipyridine,[2] and 4,4'-bis(4-bromophenyl)-6,6'-diphenyl-2,2'-bipyridine[2] were prepared as previously reported.

**_N_-[2-oxoethyl-2-naphthyl]pyridine-1-ium iodide**



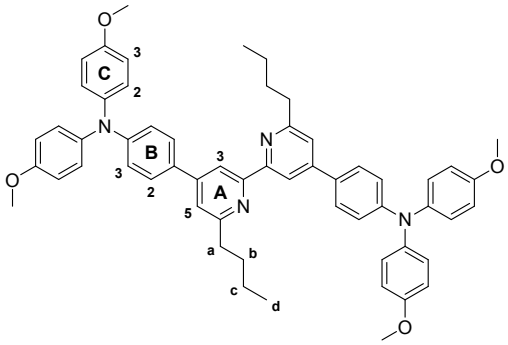

2-Naphthylmethylketone (12.0 g, 70.0 mmol) and iodine (17.3 mL, 17.8 g, 70.0 mmol) were heated in pyridine (100 mL) under reflux for 1h. The resulting orange solid was separated by filtration, washed with cold $Et_2O$ and dried under vacuum. The product was isolated as an orange solid (20.2 g, 53.8 mmol, 76.7%). The crude material was used in the next step without purification. $^1$H NMR (500 MHz, $CD_3CN$) δ/ppm: 8.77 (m, 1H, $H^{B1}$), 8.74 (m, 2H, $H^{A2}$), 8.65 (m, 1H, $H^{A4}$), 8.16 (m, 3H, $H^{A3+B3}$), 8.06 (m, 3H, $H^{B4+B5+B8}$), 7.75 (m, 1H, $H^{B7}$), 7.70 (m, 1H, $H^{B6}$), 6.42 (s, 2H, $H^{CH2}$). **$^{13}$**C NMR (126 MHz, $CD_3CN$) δ/ppm: 190.6 ($C^{C=O}$), 147.7 ($C^{A4}$), 147.1 ($C^{A2}$), **13**7.1 ($C^{B4a/B8a}$), **13**3.2 ($C^{B4a/B8a}$), **13**1.7 ($C^{B1}$), **13**0.6 ($C^{B3+B7}$), **13**0.0 ($C^{B4}$), 129.0 ($C^{A3}$), 128.8 ($C^{B8}$), 128.5 ($C^{B6}$), 123.9 ($C^{B2+B5}$), 67.3 ($C^{CH2}$).

**4,4'-Bis(4-bromophenyl)-6,6'-di-2-naphthyl-2,2'-bipyridine**



*N*-[2-Oxoethyl-2-naphthyl]pyridine-1-ium iodide (5.10 g, **13**.6 mmol) was dissolved in EtOH (60 mL) under vigorous stirring. (1*E*,5*E*)-1,6-Bis(4-bromophenyl)hexa-1,5-diene-3,4-dione (2.85 g, 6.79 mmol) and $NH_4OAc$ (5.23 g, 67. mmol) were added followed by EtOH (30 mL), propan-2-ol (100 mL) and toluene (150 mL). The reaction mixture was heated at reflux for 1 d and was then allowed to cool r.t. while being stirred. The precipitate was collected by filtration and washed with cold EtOH. The product was recrystallized twice from EtOH, then from MeOH. The product was isolated as an off-white solid (1.77 g, 2.46 mmol, 36.3%). Decomp. > 322 °C. $^1$H NMR (500 MHz, TFA-$d_1$) δ/ppm: 8.68 (d, *J* = 1.8 Hz, 2H, $H^{A3}$), 8.66 (d, *J* = 1.8 Hz, 2H, $H^{A5}$), 8.41 (d, *J* = 2.1 Hz, 2H, $H^{C1}$), 8.06 (d, *J* = 8.6 Hz, 2H, $H^{C4}$), 7.89 (overlapping d, 4H, $H^{C5+C8}$), 7.83 (dd, *J* = 8.7, 2.0 Hz, 2H, $H^{C3}$), 7.80 (m, 4H, $H^{B2}$), 7.75 (m, 4H, $H^{B3}$), 7.63 (m, 2H, $H^{C6/C7}$), 7.58 (m, 2H, $H^{C6/C7}$). **13**C NMR (126 MHz, TFA-$d_1$) δ/ppm: 162.0 ($C^{B4}$), 159.0 ($C^{A6}$), 144.6 ($C^{A4}$), **13**7.9 ($C^{C4a/C8a}$), **13**5.8 ($C^{B3}$), **13**5.2 ($C^{C4a/C8a}$), **13**4.1 ($C^{A4}$), **13**3.0 ($C^{C4}$), **13**2.2 ($C^{C1+C6/C7}$), **13**1.7 ($C^{B1}$), **13**1.2 ($C^{B2}$), **13**0.9 ($C^{C5/C8}$), **13**0.5 ($C^{C6/C7}$), **13**0.0 ($C^{C5/C8}$), 128.4 ($C^{B2}$), 126.9 ($C^{A5}$), 126.0 ($C^{A3}$), 124.3 ($C^{C3}$). IR ($\tilde{\nu}$/cm$^{-1}$): 3051 (w), 3018 (w), 2970 (w), 1589 (m), 1574 (m), 1542 (s), 1489 (m), 1405 (m), **13**79 (m), 1075 (m), 1007 (m), 863 (m), 812 (s), 785 (m), 775 (s), 757 (s), 732 (s), 718 (m), 570 (m), 470 (s). ESI MS (*m/z*): 719.1 $[M+H]^+$ (calc. 719.1). UV-VIS ($CH_2Cl_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$): λ/nm 237 (ε / dm$^3$ mol$^{-1}$ cm$^{-1}$ 73500), 263 (105300), sh 320 (24300), 350 sh (9900). UV-VIS ($CH_2Cl_2$ + 1%TFA, 1.0 × 10$^{-5}$ mol dm$^{-3}$): λ / nm 227 (ε / dm$^3$ mol$^{-1}$ cm$^{-1}$ 81700), 262 (61600), 311 (43400), 400 sh (15300). Found: C 68.93, H 3.62, N 4.01; $C_{42}H_{26}Br_2N_2 \cdot {}^1/_2H_2O$ requires C 69.34, H 3.74, N 3.85%.

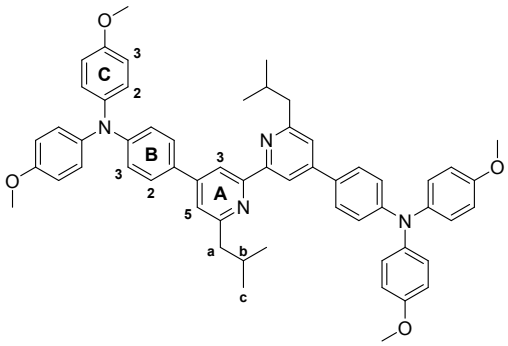
Compound **2**




4,4'-Bis(4-bromophenyl)-6,6'-di-*n*-butyl-2,2'-bipyridine (422 mg, 0.73 mmol) and bis(4-methoxyphenyl)amine (376 mg, 1.61 mmol) were suspended in dry toluene (40 mL) under argon. NaO$^t$Bu

(231 mg, 2.41 mmol) was added. A 1M toluene solution of P$^t$Bu$_3$ (29.2 μL, 0.029 mmol, 4.0 mol%) was added to a suspension of Pd(bda)$_2$ (16.8 mg, 0.029 mmol, 4.0 mol%) in dry toluene (15 mL) and the active catalyst suspension was added to the reaction mixture. The mixture was heated at 100°C for 16 h, after which time it was filtered hot. The solvent of the filtrate was removed and the resulting solid was boiled in EtOH (100 mL) until a homogeneous suspension was obtained. The solid was filtered off hot and washed with diethyl ether (30 mL). Compound **2** was isolated as yellow-green solid (563 mg, 0.64 mmol, 88 %). Mp. 165 $^o$C. $^1$H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.44 (d, *J* = 1.6 Hz, 2H, H$^{A3}$), 7.60 (d, *J* = 8.7 Hz, 4H, H$^{B2}$), 7.31 (d, *J* = 1.7 Hz, 2H, H$^{A5}$), 7.11 (d, *J* = 8.9 Hz, 8H, H$^{C2}$), 7.01 (d, *J* = 8.7 Hz, 4H, H$^{B3}$), 6.86 (d, *J* = 8.9 Hz, 8H, H$^{C3}$), 3.82 (s, 12H, OMe), 2.90 (t, *J* = 7.8 Hz, 4H, H$^a$), 1.85 – 1.78 (m, 4H, H$^b$), 1.45 (m, 4H, H$^c$), 0.97 (t, *J* = 7.4 Hz, 6H, H$^d$). **$^{13}$C** NMR (126 MHz, $CDCl_3$) δ/ppm: 162.3 (C$^{A6}$), 156.8 (C$^{A2}$), 156.3 (C$^{C4}$), 149.5 (C$^{B4}$), 148.8 (C$^{B1}$), 140.7 (C$^{C1}$), **13**0.4 (C$^{A4}$), 127.8 (C$^{B2}$), 127.1 (C$^{C2}$), 120.2 (C$^{B3}$), 119.6 (C$^{A5}$), 116.1 (C$^{A3}$), 114.9 (C$^{C3}$), 55.7 (C$^{OMe}$), 38.4 (C$^a$), 32.2 (C$^b$), 22.7 (C$^c$), 14.2 (C$^d$). IR ($\tilde{\nu}$/cm$^{-1}$): 3036 (w), 3002 (w), 2952 (w), 2926 (w), 2855 (w), 2832 (w), 1588 (m), 1501 (s), 1461 (m), 1285 (m), 1238 (s), 1178 (m), 1105 (m), 1029 (s), 823 (s), 780 (m), 662 (m), 574 (m), 527 (m). ESI MS (*m/z*): 875.5 [M+H]$^+$ (calc. 875.5). UV-VIS ($CH_2Cl_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$): $\lambda_{max}$/nm 240 sh ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 48600), 296 (41400), 359 (47500). Found: C, 78.08; H, 6.54; N, 6.31; $C_{58}H_{58}N_4O_4 \cdot H_2O$ requires C, 78.00; H, 6.77; N, 6.27.

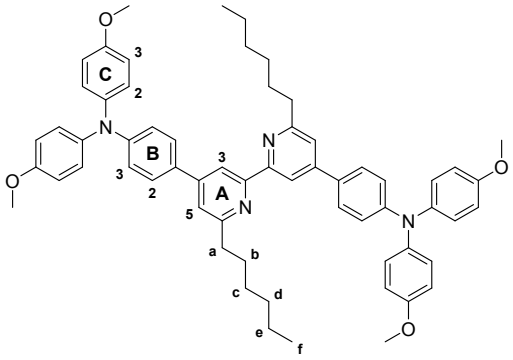
Compound **3**




Compound **3** was prepared and purified in the same manner as **2** starting with 4,4'-bis(4-bromophenyl)-6,6'-di-*iso*-butyl-2,2'-bipyridine (400 mg, 0.69 mmol), bis(4-methoxyphenyl)amine (356 mg, 1.52 mmol) and NaO$^t$Bu (219 mg, 2.28 mmol) in dry toluene (60 mL). For

the preparation of the catalyst suspension, $Pd(bda)_2$ (15.9 mg, 0.027 mmol, 4.0 mol%), dry toluene (25 mL) and 1M toluene solution of $P^tBu_3$ (27.7 μL, 0.027 mmol, 4.0 mol%) were used. The reaction time at 100°C was 16 h. Compound **3** was isolated as yellow-green solid (520 mg, 0.59 mmol, 86 %). Mp. 238 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.46 (d, *J* = 1.3 Hz, 2H, $H^{A3}$), 7.60 (d, *J* = 8.8 Hz, 4H, $H^{B2}$), 7.28 (d, *J* = 1.6 Hz, 2H, $H^{A5}$), 7.12 (d, *J* = 9.0 Hz, 8H, $H^{C2}$), 7.02 (d, *J* = 8.8 Hz, 4H, $H^{B3}$), 6.87 (d, *J* = 9.0 Hz, 8H, $H^{C3}$), 3.82 (s, 12H, $H^{OMe}$), 2.76 (d, *J* = 7.2 Hz, 4H, $H^a$), 2.26 (m, 2H, $H^b$), 0.99 (d, *J* = 6.6 Hz, 12H, $H^c$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ/ppm: 161.3 ($C^{A6}$), 156.8 ($C^{A2}$), 156.3 ($C^{C4}$), 149.6 ($C^{B4}$), 148.6 ($C^{B1}$), 140.7 ($C^{C1}$), **13**0.4 ($C^{A4}$), 127.8 ($C^{B2}$), 127.1 ($C^{C2}$), 120.4 ($C^{A5}$), 120.2 ($C^{B3}$), 116.0 ($C^{A3}$), 114.9 ($C^{C3}$), 55.7 ($C^{OMe}$), 47.9 ($C^a$), 29.2 ($C^b$), 22.7 ($C^c$). IR ($\tilde{\nu}$/cm$^{-1}$): 3063 (w), 3033 (w), 3003 (w), 2950 (w), 2926 (w), 2899 (w), 2866 (w), 2831 (w), 1587 (m), 1502 (s), **13**19 (m), 1240 (s), 1181 (m), 1166 (m), 1029 (m), 825 (s), 661 (m), 592 (m), 573 (m). ESI MS (*m/z*): 875.6 $[M+H]^+$ (calc. 875.5). UV-VIS ($CH_2Cl_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$): $\lambda_{max}$/nm 240 sh ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 48500), 296 (40400), 360 (45300). Found: C, 78.29; H, 6.63; N, 6.15; $C_{58}H_{58}N_4O_4 \cdot H_2O$ requires C, 78.00; H, 6.77; N, 6.27.

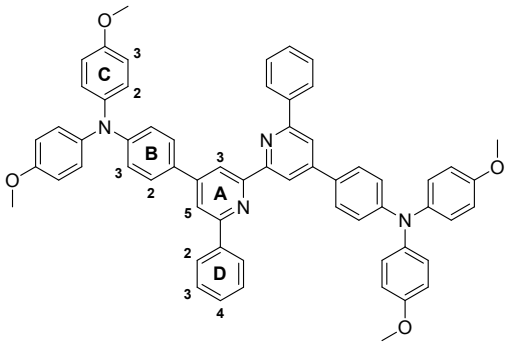
Compound **4**




Compound **4** was prepared and purified in the same manner as **2** starting with 4,4'-bis(4-bromophenyl)-6,6'-di-*n*-hexyl-2,2'-bipyridine (482 mg, 0.76 mmol), bis(4-methoxyphenyl)amine (391 mg, 1.67 mmol) and $NaO^tBu$ (241 mg, 2.51 mmol) in dry toluene (50 mL). For the preparation of the catalyst suspension one $Pd(bda)_2$ (17.5 mg, 0.030 mmol, 4.0 mol%), dry toluene (15 mL) and 1M toluene solution of $P^tBu_3$ (30.4 μL, 0.030 mmol, 4.0 mol%) were used. Reaction time at 100°C was 16 h. Compound **4** was isolated as yellow-green solid (608 mg, 0.65 mmol, 86 %). Mp. 179 °C. $^1$H NMR

(500 MHz, $CDCl_3$) δ/ppm: 8.44 (d, *J* = 1.7 Hz, 2H, $H^{A3}$), 7.60 (d, *J* = 8.8 Hz, 4H, $H^{B2}$), 7.31 (d, *J* = 1.7 Hz, 2H, $H^{A5}$), 7.11 (d, *J* = 8.9 Hz, 8H, $H^{C2}$), 7.01 (d, *J* = 8.8 Hz, 4H, $H^{B3}$), 6.87 (d, *J* = 9.0 Hz, 8H, $H^{C3}$), 3.82 (s, 12H, $H^{OMe}$), 2.89 (t, *J* = 7.8 Hz, 4H, $H^{a}$), 1.83 (m, 4H, $H^{b}$), 1.42 (m, 4H, $H^{c}$), 1.34 (m, 8H, $H^{d+e}$), 0.88 (t, *J* = 7.0 Hz, 6H, $H^{f}$). **13**C NMR (126 MHz, $CDCl_3$) δ/ppm: 162.4 ($C^{A6}$), 156.8 ($C^{A2}$), 156.3 ($C^{C4}$), 149.5 ($C^{B4}$), 148.9 ($C^{B1}$), 140.7 ($C^{C1}$), **13**0.4 ($C^{A4}$), 127.8 ($C^{B2}$), 127.0 ($C^{C2}$), 120.2 ($C^{B3}$), 119.6 ($C^{A5}$), 116.1 ($C^{A3}$), 114.9 ($C^{C3}$), 55.7 ($C^{OMe}$), 38.7 ($C^{a}$), 32.0 ($C^{d/e}$), 30.0 ($C^{b}$), 29.3 ($C^{c}$), 22.8 ($C^{d/e}$), 14.3 ($C^{f}$). IR ($\tilde{\nu}$/$cm^{-1}$): 3036 (w), 2997 (w), 2950 (w), 2921 (w), 2851 (w), 2827 (w), 1591 (m), 1504 (s), 1461 (m), 1439 (m), **13**21 (m), 1291 (m), 1239 (s), 1194 (m), 1167 (m), 1038 (m), 826 (s), 660 (m), 597 (m), 571 (m), 530 (m). ESI MS (*m/z*): 931.6 $[M+H]^+$ (calc. 931.5). UV-VIS ($CH_2Cl_2$, 1.0 × $10^{-5}$ mol $dm^{-3}$): $\lambda_{abs}$/nm 240 sh ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 47300), 297 (41100), 359 (46600). Found: C, 77.22; H, 6.91; N, 5.99; $C_{62}H_{66}N_4O_4 \cdot 2H_2O$ requires C, 76.99; H, 7.29; N, 5.79.

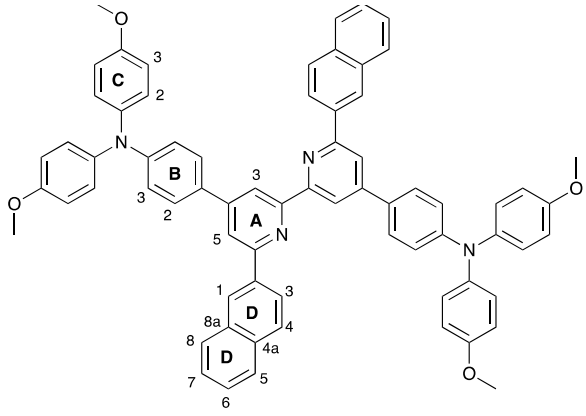
Compound **5**




Compound **5** was prepared and purified in the same manner as **2** starting with 4,4'-bis(4-bromophenyl)-6,6'-diphenyl-2,2'-bipyridine (432 mg, 0.70 mmol), bis(4-methoxyphenyl)amine (359 mg, 1.54 mmol) and NaO*t*Bu (221 mg, 2.30 mmol) in dry toluene (50 mL). For the preparation of the catalyst suspension, $Pd(bda)_2$ (16.1 mg, 0.028 mmol, 4.0 mol%), dry toluene (15 mL) and 1M toluene solution of P*t*$Bu_3$ (29.7 μL, 0.028 mmol, 4.0 mol%) were used. The reaction time at 100°C was 16 h. Compound **5** was isolated as yellow-green solid (552 mg, 0.60 mmol, 86 %). Decomp. >172 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.82 (d, *J* = 1.4 Hz, 2H, $H^{A3}$), 8.22 (d, *J* = 7.2 Hz, 4H, $H^{D2}$), 7.95 (d, *J* = 1.4 Hz, 2H, $H^{A5}$), 7.69 (d, *J* = 8.8 Hz, 4H, $H^{B2}$), 7.54 (m, 4H, $H^{D3}$), 7.45 (m, 2H, $H^{D4}$), 7.15 (d, *J* = 8.9 Hz, 8H, $H^{C2}$), 7.06 (d, *J* = 8.7 Hz, 4H, $H^{B3}$), 6.89 (d, *J* = 9.0 Hz, 8H, $H^{C3}$), 3.83 (s, 12H, $H^{OMe}$). **13**C NMR (126 MHz, $CDCl_3$)

δ/ppm: 157.0 ($C^{A6}$), 156.7 ($C^{A2}$), 156.4 ($C^{C4}$), 149.8 ($C^{B4}$), 149.7 ($C^{B1}$), 140.6 ($C^{C1}$), 140.0 ($C^{D1}$), **13**0.2 ($C^{A4}$), 128.8 ($C^{D4}$), 128.4 ($C^{D3}$), 127.9 ($C^{B2}$), 127.2 ($C^{D2}$), 127.2 ($C^{C2}$), 120.1 ($C^{B3}$), 117.8 ($C^{A5}$), 117.2 ($C^{A3}$), 115.0 ($C^{C3}$), 55.7 ($C^{OMe}$). IR ($\tilde{\nu}$/cm$^{-1}$): 3033 (w), 2952 (w), 2929 (w), 2903 (w), 2832 (w), 1590 (m), 1503 (s), 1462 (m), 1441 (m), 1239 (s), 1194 (m), 1180 (m), 1165 (m), 1032 (m), 824 (m), 774 (m), 688 (m), 660 (m), 576 (m), 537 (m). ESI MS (*m/z*): 915.5 $[M+H]^+$ (calc. 915.4). UV-VIS ($CH_2Cl_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$): $\lambda_{max}$/nm 254 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 60500), 290 sh (44100), 369 (37300). Found: C, 78.08; H, 5.36; N, 5.88; $C_{62}H_{50}N_4O_4 \cdot H_2O$ requires C, 78.29; H, 5.72; N, 5.89.

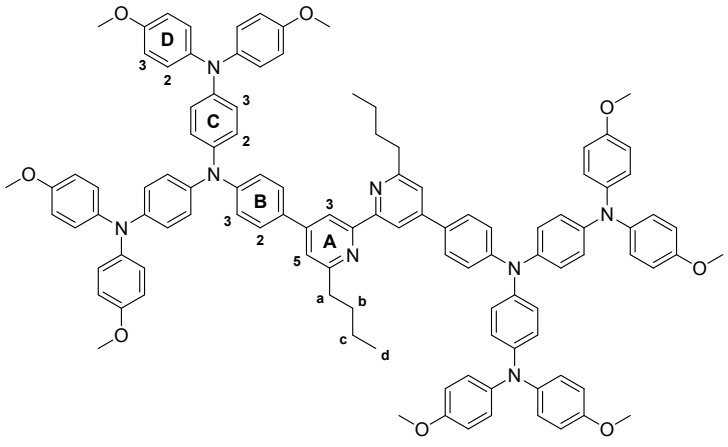
Compound **6**




Compound **6** was prepared and purified in the same manner as **2** starting with 4,4'-bis(4-bromophenyl)-6,6'-di(naphthalen-2-yl)-2,2'-bipyridine (460 mg, 0.64 mmol), bis(4-methoxyphenyl)amine (330 mg, 1.41 mmol) and NaO$^t$Bu (203 mg, 2.11 mmol) in dry toluene (70 mL). For the preparation of the catalyst suspension, $Pd(bda)_2$ (14.7 mg, 0.026 mmol, 4.0 mol%), dry toluene (10 mL) and 1M toluene solution of P$^t$Bu$_3$ (25.6 μL, 0.026 mmol, 4.0 mol%) were used. The reaction time at 100°C was 24 h. Compound **6** was isolated as yellow-green solid (393 mg, 0.39 mmol, 60%). Decomp. >320 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.89 (d, *J* = 1.5 Hz, 2H, $H^{A3}$), 8.65 (m, 2H, $H^{D1}$), 8.42 (dd, *J* = 8.6, 1.7 Hz, 2H, $H^{D3}$), 8.11 (d, *J* = 1.6 Hz, 2H, $H^{A5}$), 8.01 (m, 4H, $H^{D4+D5/D8}$), 7.91 (m, 2H, $H^{D5/D8}$), 7.75 (d, *J* = 8.8 Hz, 4H, $H^{B2}$), 7.53 (m, 4H, $H^{D6+D7}$), 7.16 (d, *J* = 9.0 Hz, 8H, $H^{C2}$), 7.09 (d, *J* = 8.8 Hz, 4H, $H^{B3}$), 6.89 (d, *J* = 9.0 Hz, 8H, $H^{C3}$), 3.83 (s, 12H, $H^{OMe}$). **13**C NMR (126 MHz, $CDCl_3$) δ/ppm: 157.0 ($C^{A6}$), 156.9 ($C^{A2}$), 156.4 ($C^{C4}$), 149.9 ($C^{B4}$), 149.8 ($C^{B1}$), 140.6 ($C^{C1}$), **13**7.4 ($C^{D2}$),

**13**3.8 ($C^{D4a}$), **13**3.7 ($C^{D8a}$), **13**0.2 ($C^{A4}$), 128.9 ($C^{D4/D5/D8}$), 128.5 ($C^{D4/D5/D8}$), 128.0 ($C^{B2}$), 127.9 ($C^{D5/D8}$), 127.2 ($C^{C2}$), 126.6 ($C^{D6/D7}$), 126.5 ($C^{D1}$), 126.4 ($C^{D6/D7}$), 125.2 ($C^{D3}$), 120.2 ($C^{B3}$), 118.2 ($C^{A5}$), 117.4 ($C^{A3}$), 115.0 ($C^{C3}$), 55.7 ($C^{OMe}$). IR ($\tilde{\nu}$/cm$^{-1}$): 3059 (w), 3038 (w), 2999 (w), 2950 (w), 2929 (w), 2905 (w), 2830 (w), 1587 (m), 1502 (s), 1463 (m), 1439 (m), 1283 (m), 1239 (s), 1180 (m), 1035 (m), 820 (s), 755 (m), 575 (m), 533 (m), 476 (m). ESI MS (*m/z*): 1015.5 $[M+H]^+$ (calc. 1015.4). UV-VIS ($CH_2Cl_2$, 1.0 × $10^{-5}$ mol dm$^{-3}$): $\lambda_{abs}$/nm 234 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 84000), 255 (82900), 297 (55400), 370 (36500). Found: C, 79.28; H, 5.30; N, 5.47; $C_{70}H_{54}N_4O_4 \cdot 2.5H_2O$ requires C, 79.30; H, 5.61; N, 5.28.

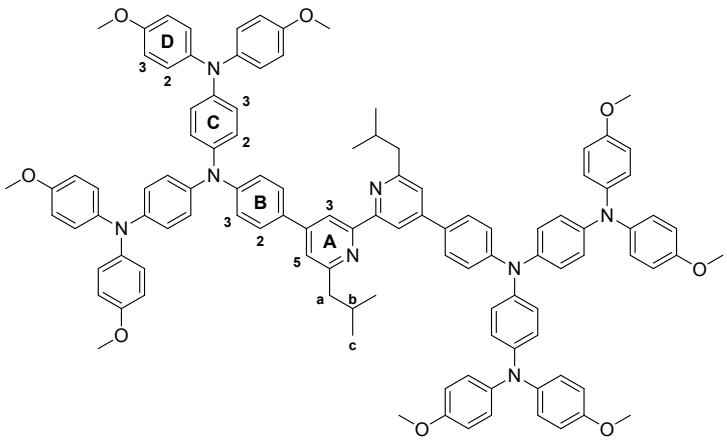
Compound **8**




4,4'-Bis(4-bromophenyl)-6,6'-di-*n*-butyl-2,2'-bipyridine (69.9 mg, 0.12 mmol), 4,4'-bis(N,N-bis(4-methoxyphenyl)amino)diphenylamine (166 mg, 0.26 mmol) and NaO$^t$Bu (63.9 mg, 0.67 mmol) were suspended in in dry toluene (30 mL). A 1M solution of P$^t$Bu$_3$ in toluene (10.0 μL, 0.012 mmol, 10 mol%) was added to a suspension of Pd(bda)$_2$ (6.95 mg, 0.012 mmol, 10 mol%) in dry toluene (10 mL). The freshly prepared catalyst suspension was added to the reaction mixture which was then heated to 100°C for 16 h. The reaction mixture was filtered hot to remove insoluble solids. The solvent was removed and the resulting solid was boiled in EtOH until a homogeneous suspension was obtained. After filtration

compound **8** was isolated as yellow-green solid (143 mg, 85.9 μmol, 71 %). Decomp. > 305 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.46 (d, *J* = 1.7 Hz, 2H, $H^{A3}$), 7.62 (d, *J* = 8.8 Hz, 4H, $H^{B2}$), 7.32 (d, *J* = 1.7 Hz, 2H, $H^{A5}$), 7.11 (d, *J* = 8.7 Hz, 4H, $H^{B3}$), 7.07 (d, *J* = 8.9 Hz, 16H, $H^{D2}$), 7.00 (d, *J* = 8.9 Hz, 8H, $H^{C2}$), 6.90 (d, *J* = 8.9 Hz, 8H, $H^{C3}$), 6.83 (d, *J* = 9.0 Hz, 16H, $H^{D3}$), 3.80 (s, 24H, $H^{OMe}$), 2.90 (t, *J* = 7.8 Hz, 4H, $H^{a}$), 1.82 (m, 4H, $H^{b}$), 1.54–1.40 (m, 4H, $H^{c}$), 0.98 (t, *J* = 7.3 Hz, 6H, $H^{d}$). **13**C NMR (126 MHz, $CDCl_3$, 25°C, TMS) δ/ppm: 162.3 ($C^{A6}$), 156.8 ($C^{A2}$), 155.7 ($C^{D4}$), 149.2 ($C^{B4}$), 148.8 ($C^{B1}$), 144.8 ($C^{C4}$), 141.4 ($C^{D1}$), 140.5 ($C^{C1}$), **13**0.7 ($C^{A4}$), 127.8 ($C^{B2}$), 126.2 ($C^{D2+C2}$), 122.3 ($C^{C3}$), 120.9 ($C^{B3}$), 119.6 ($C^{A5}$), 116.1 ($C^{A3}$), 114.8 ($C^{D3}$), 55.6 ($C^{OMe}$), 38.5 ($C^{a}$), 32.2 ($C^{b}$), 22.7 ($C^{c}$), 14.2 ($C^{d}$). IR ($\tilde{\nu}$/cm$^{-1}$): 3038 (w), 2997 (w), 2929 (w), 2833 (w), 1591 (m), 1499 (s), 1238 (s), 1038 (m), 825 (s), 574 (m), 527 (m). ESI MS (*m/z*): 832.3 $[M+2H]^{2+}$, (calc. 832.4). UV-VIS ($CH_2Cl_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$): $\lambda_{max}$/nm 226 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 92100), 307 (87600), 343 (73800). Found: C, 77.25; H, 5.95; N, 6.66; $C_{110}H_{102}N_8O_8 \cdot 2H_2O$ requires C, 77.71; H, 6.28; N, 6.59.

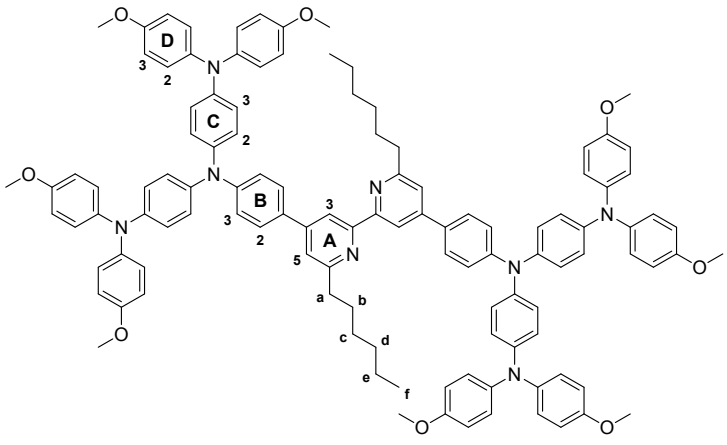
Compound **9**




Compound **9** was prepared and purified in the same manner as **8** starting with 4,4'-bis(4-bromophenyl)-6,6'-di-isobutyl-2,2'-bipyridine (196 mg, 0.34 mmol), 4,4'-bis(N,N-bis(4-methoxyphenyl)amino)diphenylamine (466 mg, 0.75 mmol) and NaO$^t$Bu (185 mg, 1.87 mmol) in dry toluene (60 mL). For the preparation of

the catalyst suspension, $Pd(bda)_2$ (19.5 mg, 0.034 mmol, 10 mol%), dry toluene (20 mL) and 1M toluene solution of $P^tBu_3$ (34.0 μL, 0.034 mmol, 10 mol%) were used. The reaction time at 100°C was 16 h. Compound **9** was isolated as yellow-green solid (382 mg, 0.23 mmol, 68 %). Decomp. > 340 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.46 (d, *J* = 1.6 Hz, 2H, $H^{A3}$), 7.62 (d, *J* = 8.7 Hz, 4H, $H^{B2}$), 7.28 (d, *J* = 1.6 Hz, 2H, $H^{A5}$), 7.11 (d, *J* = 8.4 Hz, 4H, $H^{B3}$), 7.07 (d, *J* = 9.0 Hz, 16H, $H^{D2}$), 7.00 (d, *J* = 8.7 Hz, 8H, $H^{C2}$), 6.89 (d, *J* = 8.9 Hz, 8H, $H^{C3}$), 6.83 (d, *J* = 9.0 Hz, 16H, $H^{D3}$), 3.80 (s, 24H, $H^{OMe}$), 2.76 (d, *J* = 7.2 Hz, 4H, $H^a$), 2.26 (m, 2H, $H^b$), 0.99 (d, *J* = 6.6 Hz, 12H, $H^c$). **13**C NMR (126 MHz, $CDCl_3$) δ/ppm: 161.3 ($C^{A6}$), 156.8 ($C^{A2}$), 155.7 ($C^{D4}$), 148.6 ($C^{B1, B4}$), 144.8 ($C^{C4}$), 141.4 ($C^{D1}$), 140.5 ($C^{C1}$), **13**0.5 ($C^{A4}$), 127.8 ($C^{B2}$), 126.2 ($C^{D2, C2}$), 122.3 ($C^{C3}$), 120.9 ($C^{B3}$), 120.4 ($C^{A5}$), 116.0 ($C^{A3}$), 114.8 ($C^{D3}$), 55.6 ($C^{OMe}$), 47.9 ($C^a$), 29.2 ($C^b$), 22.7 ($C^c$). IR ($\tilde{\nu}$/cm$^{-1}$): 3038 (w), 2997 (w), 2952 (w), 2924 (w), 2903 (w), 2866 (w), 2830 (w), 1590 (m), 1499 (s), 1238 (s), 1036 (m), 825 (s), 574 (m), 526 (m). ESI MS (*m/z*): 1665.6 $[M+H]^+$, (calc. 1664.8), 832.8 $[M+2H]^{2+}$ (calc. 832.9). UV-VIS ($CH_2Cl_2$, 1.0 × $10^{-5}$ mol dm$^{-3}$): $\lambda_{max}$/nm: 227 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 96300), 307 (91200), 344 (77800). Found: C, 78.97; H, 6.21; N, 6.79; $C_{110}H_{102}N_8O_8 \cdot {}^1/_2H_2O$ requires C, 78.97; H, 6.21; N, 6.70.

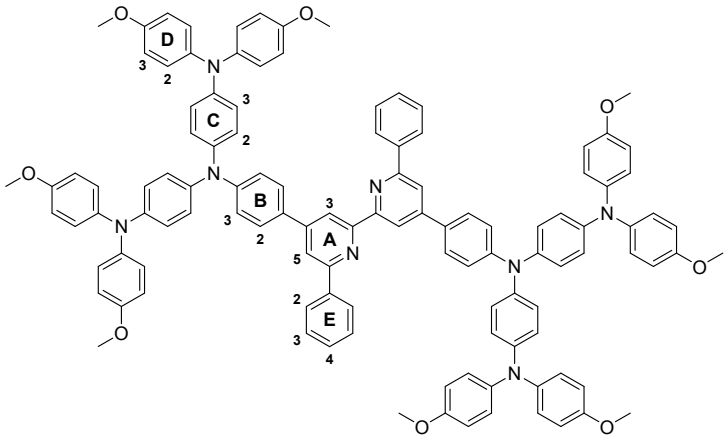
Compound **10**




Compound **10** was prepared and purified in the same manner as **8** starting with 4,4'-bis(4-bromophenyl)-6,6'-di-*n*-hexyl-2,2'-bipyridine (182 mg, 0.29 mmol),

4,4'-bis(N,N-bis(4-methoxyphenyl)amino)diphenylamine (394 mg, 0.63 mmol) and NaO$^t$Bu (156 mg, 1.58 mmol) in dry toluene (50 mL). For the preparation of the catalyst suspension one Pd(bda)$_2$ (16.5 mg, 0.029 mmol, 10 mol%), dry toluene (10 mL) and 1M toluene solution of P$^t$Bu$_3$ (29.0 μL, 0.029 mmol, 10 mol%) were used. The reaction time at 100°C was 16 h. Compound **10** was isolated as yellow-green solid (399 mg, 0.23 mmol, 81 %). Decomp. > 265 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.46 (d, *J* = 1.7 Hz, 2H, H$^{A3}$), 7.62 (d, *J* = 8.8 Hz, 4H, H$^{B2}$), 7.32 (d, *J* = 1.7 Hz, 2H, H$^{A5}$), 7.11 (d, *J* = 8.8 Hz, 4H, H$^{B3}$), 7.07 (d, *J* = 9.0 Hz, 16H, H$^{D2}$), 7.00 (d, *J* = 8.8 Hz, 8H, H$^{C2}$), 6.90 (d, *J* = 8.9 Hz, 8H, H$^{C3}$), 6.83 (d, *J* = 9.0 Hz, 16H, H$^{D3}$), 3.80 (s, 24H, H$^{OMe}$), 2.90 (t, *J* = 7.7 Hz, 4H, H$^a$), 1.84 (m, 4H, H$^b$), 1.44 (m, 4H, H$^c$), 1.35 (m, 8H, H$^{d+e}$), 0.89 (t, *J* = 7.1 Hz, 6H, H$^f$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ/ppm: 162.3 (C$^{A6}$), 156.8 (C$^{A2}$), 155.7 (C$^{D4}$), 148.8 (C$^{B1, B4}$), 144.8 (C$^{C4}$), 141.3 (C$^{D1}$), 140.5 (C$^{C1}$), **13**0.4 (C$^{A4}$), 127.8 (C$^{B2}$), 126.2 (C$^{D2, C2}$), 122.3 (C$^{C3}$), 120.9 (C$^{B3}$), 119.6 (C$^{A5}$), 116.1 (C$^{A3}$), 114.8 (C$^{D3}$), 55.6 (C$^{OMe}$), 38.7 (C$^a$), 32.0 (C$^{d/e}$), 30.0 (C$^b$), 29.3 (C$^c$), 22.8 (C$^{d/e}$), 14.3 (C$^f$). IR ($\tilde{\nu}$/cm$^{-1}$): 3036 (w), 2999 (w), 2950 (w), 2928 (w), 2853 (w), 2833 (w), 1591 (m), 1497 (s), 1237 (s), 1036 (m), 824 (s), 572 (m), 523 (m). ESI MS (*m/z*): 1720.5 [M+H]$^+$, (calc. 1720.9), 860.3 [M+2H]$^{2+}$ (calc. 860.95). UV-VIS ($CH_2Cl_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$): $\lambda_{max}$/nm 227 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 99300), 308 (96000), 343 (82600). Found: C, 79.06; H, 6.58; N, 6.55; $C_{114}H_{110}N_8O_8 \cdot {}^1/_2H_2O$ requires C, 79.18; H, 6.47; N, 6.48.

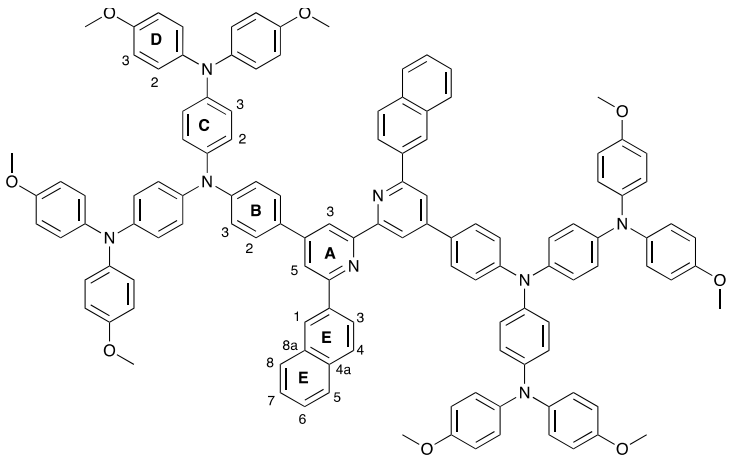
Compound **11**



Compound **11** was prepared and purified in the same manner as **8** starting with 4,4'-bis(4-bromophenyl)-6,6'-diphenyl-2,2'-bipyridine (49.1 mg, 79.4 μmol), 4,4'-bis(N,N-bis(4-methoxyphenyl)amino)diphenylamine (109 mg, 175 μmol) and NaO$^t$Bu (41.9 mg, 436 μmol) in dry toluene (50 mL). For the preparation of the catalyst suspension, Pd(bda)$_2$ (4.56 mg, 7.94 μmol, 10 mol%), dry toluene (10 mL) and 1M toluene solution of P$^t$Bu$_3$ (7.94 μL, 7.94 μmol, 10 mol%) were used. The reaction time at 100°C was 16 h. Compound **11** was isolated as yellow-green solid (88.0 mg, 51.6 μmol, 65%). Decomp. > 321 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ /ppm: 8.83 (d, *J* = 1.7 Hz, 2H, H$^{A3}$), 8.23 (d, *J* = 7.2 Hz, 4H, H$^{E3}$), 7.96 (d, *J* = 1.7 Hz, 2H, H$^{A3}$), 7.71 (d, *J* = 8.8 Hz, 4H, H$^{B2}$), 7.54 (dd, *J* = 7.4 Hz, 4H, H$^{E3}$), 7.50 – 7.44 (m, 2H, H$^{E4}$), 7.16 (d, *J* = 8.6 Hz, 4H, H$^{B3}$), 7.08 (d, *J* = 8.9 Hz, 16H, H$^{D2}$), 7.03 (d, *J* = 8.9 Hz, 8H, H$^{C2}$), 6.92 (d, *J* = 8.8 Hz, 8H, H$^{C3}$), 6.84 (d, *J* = 9.0 Hz, 16H, H$^{D3}$), 3.80 (s, 24H, H$^{OMe}$). **$^{13}$**C NMR (126 MHz, $CDCl_3$) δ/ppm: 157.00 (C$^{A6}$), 156.8 (C$^{A2}$), 155.7 (C$^{D4}$), 149.7 (C$^{B4}$), 149.5 (C$^{B1}$), 145.0 (C$^{C4}$), 141.3 (C$^{D1}$), 140.3 (C$^{C1}$), 140.0 (C$^{E1}$), **13**0.4 (C$^{A4}$), 128.9 (C$^{E4}$), 128.8 (C$^{E3}$), 127.9 (C$^{B2}$), 127.3 (C$^{E2}$), 126.3 (C$^{C2, D2}$), 122.2 (C$^{C3}$), 120.7 (C$^{B3}$), 117.9 (C$^{A5}$), 117.3 (C$^{A3}$), 114.8 (C$^{D3}$), 55.7 (C$^{OMe}$). IR ($\tilde{\nu}$/cm$^{-1}$): 3037 (w), 2998 (w), 2949 (w), 2926 (w), 2900 (w), 2832 (w), 1591 (m), 1495 (s), 1235 (s), 1034 (m), 822 (s), 575 (m), 522 (m). ESI MS

(*m/z*): 852.4 $[M+2H]^{2+}$ (calc. 852.7). UV-VIS ($CH_2Cl_2$, 1.0 × $10^{-5}$ mol $dm^{-3}$): $\lambda_{max}$/nm 227 ($\varepsilon$ / $dm^3$ $mol^{-1}$ $cm^{-1}$ **13**3100), 310 (118800), 400 sh (44100). Found: C, 77.15; H, 5.46; N, 6.29; $C_{114}H_{94}N_8O_8 \cdot 4H_2O$ requires C, 77.09; H, 5.79; N, 6.31.

Compound **12**




Compound **12** was prepared and purified in the same manner as **8** starting with 4,4'-bis(4-bromophenyl)-6,6'-di-2-naphthyl-2,2'-bipyridine (240 mg, 0.34 mmol), 4,4'-bis(N,N-bis(4-methoxyphenyl)amino)diphenylamine (459 mg, 0.74 mmol) and NaO$^t$Bu (182 mg, 1.84 mmol) in dry toluene (100 mL). For the preparation of the catalyst suspension, $Pd(bda)_2$ (19.2 mg, 33.5 mol, 10 mol%), dry toluene (20 mL) and 1M toluene solution of P$^t$Bu$_3$ (33.5 µL, 33.5 mol, 10 mol%) were used. The reaction time at 100°C was 16 h. Compound **12** was isolated as a yellow solid (432 mg, 0.24 mmol, 72%). Mp. 333 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ /ppm: 8.93 (d, *J* = 1.7 Hz, 2H, $H^{A3}$), 8.64 (d, *J* = 1.7 Hz, 2H, $H^{E1}$), 8.43 (dd, *J* = 8.6, 1.8 Hz, 2H, $H^{E3}$), 8.12 (d, *J* = 1.6 Hz, 2H, $H^{A5}$), 8.02 (m, 4H, $H^{E4+E5/E8}$), 7.92 (m, 2H, $H^{E5/E8}$), 7.77 (d, *J* = 8.7 Hz, 4H, $H^{B2}$), 7.54 (m, 4H, $H^{E6+E7}$), 7.18 (d, *J* = 8.8 Hz, 4H, $H^{B3}$), 7.08 (d, *J* = 9.0 Hz, 16H, $H^{D2}$), 7.04 (d, *J* = 9.0 Hz, 8H, $H^{C2}$), 6.92 (d,

*J* = 9.0 Hz, 8H, $H^{C3}$), 6.84 (d, *J* = 8.9 Hz, 16H, $H^{D3}$), 3.80 (s, 24H, $H^{OMe}$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ/ppm: 157.0 ($C^{A2+A6}$), 155.7 ($C^{D4}$), 149.9 ($C^{B1}$), 149.5 ($C^{B4}$), 145.0 ($C^{C4}$), 141.3 ($C^{D1}$), 140.3 ($C^{C1}$), **13**7.4 ($C^{E2}$), **13**3.7 ($C^{E4a+E8a}$), **13**0.4 ($C^{A4}$), 128.9 ($2C^{E4+E5/E8}$), 128.0 ($C^{B2}$), 127.6 ($C^{E5/E8}$), 126.4 ($C^{E1+E6+E7}$), 125.2 ($C^{E3}$), 122.2 ($C^{C3}$), 120.8 ($C^{B3}$), 118.1 ($C^{A5}$), 117.3 ($C^{A3}$), 114.6 ($C^{D3}$), 55.7 ($C^{OMe}$). IR ($\tilde{\nu}$/$cm^{-1}$): 3038 (w), 2994 (w), 2947 (w), 2931 (w), 2900 (w), 2832 (w), 1599 (m), 1587 (m), 1495 (s), 1235 (s), 1034 (m), 822 (s), 575 (m), 523 (m), 471 (m). ESI MS (*m/z*): 1804.6 $[M+H]^+$, (calc. 1804.8), 902.9 $[M+2H]^{2+}$ (calc. 902.4). UV-VIS ($CH_2Cl_2$, 1.0 × $10^{-5}$ mol $dm^{-3}$): $\lambda_{max}$/nm 228 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 165000), 306 (140300), 400 sh (49800). Found: C, 80.26; H, 5.48; N, 6.18; $C_{122}H_{98}N_8O_8 \cdot H_2O$ requires C, 80.42; H, 5.53; N, 6.15.

Table S1. DSC performance data (including duplicate masked cells) using anchoring ligand **13** and first-generation ancillary ligands, and acetone in the $[CuL_2]$+ dipping cycle. Relative efficiencies (last column) are with respect to 100% for standard dye N719 measured under the same conditions. $V_{OC}$ = open circuit voltage, $J_{SC}$ = short circuit current density, *ff* = fill factor.

| Anchored dye | $J_{sc}$ / mA cm$^{-2}$ | $V_{oc}$ / mV | ff / % | η / % | Rel. η / % |
|---|---|---|---|---|---|
| On the day of sealing the cell | | | | | |
| [Cu(**13**)(**1**)]$^+$ | 5.70 | 513 | 71.7 | 2.10 | 28.7 |
| [Cu(**13**)(**1**)]$^+$ | 6.00 | 510 | 70.3 | 2.15 | 29.4 |
| [Cu(**13**)(**2**)]$^+$ | 4.51 | 485 | 68.8 | 1.50 | 20.5 |
| [Cu(**13**)(**2**)]$^+$ | 4.41 | 482 | 69.4 | 1.48 | 20.2 |
| [Cu(**13**)(**3**)]$^+$ | 3.64 | 470 | 68.7 | 1.18 | 16.1 |
| [Cu(**13**)(**3**)]$^+$ | 4.22 | 475 | 69.6 | 1.39 | 19.0 |
| [Cu(**13**)(**4**)]$^+$ | 5.63 | 521 | 71.3 | 2.09 | 28.6 |
| [Cu(**13**)(**4**)]$^+$ | 5.60 | 542 | 71.8 | 2.18 | 29. 8 |
| [Cu(**13**)(**5**)]$^+$ | 2.76 | 468 | 65.8 | 0.85 | 11.6 |
| [Cu(**13**)(**5**)]$^+$ | 3.22 | 468 | 68.6 | 1.03 | 14.1 |
| [Cu(**13**)(**6**)]$^+$ | 4.28 | 510 | 68.3 | 1.49 | 20.4 |
| [Cu(**13**)(**6**)]$^+$ | 4.29 | 508 | 67.0 | 1.46 | 19.9 |
| N719 | 16.72 | 641 | 68.4 | 7.32 | 100 |
| 1 day after sealing the cells | | | | | |
| [Cu(**13**)(**1**)]$^+$ | 4.85 | 517 | 72.1 | 1.81 | 24.5 |
| [Cu(**13**)(**1**)]$^+$ | 5.29 | 513 | 71.3 | 1.94 | 26.3 |
| [Cu(**13**)(**2**)]$^+$ | 4.17 | 475 | 68.1 | 1.35 | 18.3 |
| [Cu(**13**)(**2**)]$^+$ | 4.42 | 487 | 68.8 | 1.48 | 20.0 |
| [Cu(**13**)(**3**)]$^+$ | 3.58 | 462 | 68.0 | 1.12 | 15.2 |
| [Cu(**13**)(**3**)]$^+$ | 3.96 | 469 | 69.8 | 1.30 | 17.6 |
| [Cu(**13**)(**4**)]$^+$ | 5.53 | 523 | 70.8 | 2.05 | 27.7 |
| [Cu(**13**)(**4**)]$^+$ | 5.50 | 542 | 71.3 | 2.13 | 28.8 |
| [Cu(**13**)(**5**)]$^+$ | 2.95 | 466 | 67.0 | 0.92 | 12.4 |
| [Cu(**13**)(**5**)]$^+$ | 3.30 | 464 | 68.7 | 1.05 | 14.2 |
| [Cu(**13**)(**6**)]$^+$ | 4.05 | 506 | 62.8 | 1.29 | 17.5 |
| [Cu(**13**)(**6**)]$^+$ | 4.39 | 505 | 66.6 | 1.48 | 20.0 |
| N719 | 16.61 | 652 | 68.2 | 7.39 | 100 |
| 22 days after sealing the cells[a] | | | | | |
| [Cu(**13**)(**1**)]$^+$ | 5.27 | 520 | 71.1 | 1.94 | 24.4 |
| [Cu(**13**)(**2**)]$^+$ | 4.42 | 516 | 70.7 | 1.61 | 20.3 |
| [Cu(**13**)(**3**)]$^+$ | 4.18 | 487 | 69.6 | 1.42 | 17.9 |
| [Cu(**13**)(**4**)]$^+$ | 5.05 | 532 | 70.8 | 1.90 | 23.9 |
| [Cu(**13**)(**5**)]$^+$ | 4.00 | 485 | 69.9 | 1.36 | 17.1 |
| [Cu(**13**)(**6**)]$^+$ | 4.10 | 504 | 68.0 | 1.41 | 17.7 |
| N719 | 16.65 | 671 | 71.2 | 7.95 | 100 |

[a]For [Cu(**13**)(**1**)]$^+$, the second measurements were made after 18 days.

Table S2. DSC performance data for duplicate masked cells using anchoring ligand **13** and second-generation ancillary ligands, and acetone in the $[CuL_2]^+$ dipping cycle. Relative efficiencies (last column) are with respect to 100% for standard dye N719 measured under the same conditions. $V_{OC}$ = open circuit voltage, $J_{SC}$ = short circuit current density, *ff* = fill factor.

| Anchored dye | $J_{sc}$ / mA cm$^{-2}$ | $V_{oc}$ / mV | ff / % | η / % | Rel. η / % |
|---|---|---|---|---|---|
| On the day of sealing the cell | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 6.21 | 516 | 67.9 | 2.18 | 31.6 |
| [Cu(**13**)(**7**)]$^+$ | 6.46 | 515 | 67.9 | 2.26 | 32.8 |
| [Cu(**13**)(**8**)]$^+$ | 6.24 | 502 | 70.2 | 2.20 | 31.9 |
| [Cu(**13**)(**8**)]$^+$ | 6.08 | 506 | 70.8 | 2.18 | 31.6 |
| [Cu(**13**)(**9**)]$^+$ | 4.80 | 479 | 70.1 | 1.61 | 23.3 |
| [Cu(**13**)(**9**)]$^+$ | 5.48 | 475 | 69.9 | 1.82 | 26.4 |
| [Cu(**13**)(**10**)]$^+$ | 5.10 | 491 | 70.4 | 1.77 | 25.7 |
| [Cu(**13**)(**10**)]$^+$ | 5.25 | 488 | 70.9 | 1.81 | 26.2 |
| [Cu(**13**)(**11**)]$^+$ | 3.80 | 464 | 68.6 | 1.21 | 17.5 |
| [Cu(**13**)(**11**)]$^+$ | 4.01 | 459 | 70.2 | 1.29 | 18.7 |
| [Cu(**13**)(**12**)]$^+$ | 2.88 | 437 | 68.0 | 0.86 | 12.5 |
| [Cu(**13**)(**12**)]$^+$ | 3.04 | 444 | 69.2 | 0.93 | 13.5 |
| N719 | 16.52 | 608 | 68.8 | 6.90 | 100 |
| 1 day after sealing the cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 6.23 | 536 | 68.5 | 2.28 | |
| [Cu(**13**)(**7**)]$^+$ | 6.41 | 535 | 67.7 | 2.32 | |
| [Cu(**13**)(**8**)]$^+$ | 6.25 | 518 | 70.1 | 2.27 | |
| [Cu(**13**)(**8**)]$^+$ | 6.12 | 521 | 70.5 | 2.25 | |
| [Cu(**13**)(**9**)]$^+$ | 4.95 | 489 | 70.8 | 1.71 | |
| [Cu(**13**)(**9**)]$^+$ | 5.63 | 490 | 71.6 | 1.97 | |
| [Cu(**13**)(**10**)]$^+$ | 5.14 | 504 | 70.3 | 1.82 | |
| [Cu(**13**)(**10**)]$^+$ | 5.19 | 501 | 70.6 | 1.83 | |
| [Cu(**13**)(**11**)]$^+$ | 4.19 | 479 | 69.3 | 1.39 | |
| [Cu(**13**)(**11**)]$^+$ | 4.35 | 467 | 70.7 | 1.44 | |
| [Cu(**13**)(**12**)]$^+$ | 3.27 | 448 | 68.2 | 1.00 | |
| [Cu(**13**)(**12**)]$^+$ | 3.00 | 449 | 68.3 | 0.92 | |
| 2 days after sealing the cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 6.14 | 533 | 69.8 | 2.29 | |
| [Cu(**13**)(**7**)]$^+$ | 6.13 | 534 | 68.7 | 2.25 | |
| [Cu(**13**)(**8**)]$^+$ | 5.93 | 509 | 70.8 | 2.14 | |
| [Cu(**13**)(**8**)]$^+$ | 6.02 | 519 | 71.0 | 2.22 | |
| [Cu(**13**)(**9**)]$^+$ | 4.76 | 488 | 71.1 | 1.65 | |
| [Cu(**13**)(**9**)]$^+$ | 5.60 | 492 | 69.9 | 1.93 | |
| [Cu(**13**)(**10**)]$^+$ | 4.91 | 500 | 70.6 | 1.73 | |
| [Cu(**13**)(**10**)]$^+$ | 5.05 | 499 | 70.5 | 1.78 | |
| [Cu(**13**)(**11**)]$^+$ | 4.09 | 476 | 69.8 | 1.36 | |
| [Cu(**13**)(**11**)]$^+$ | 4.34 | 463 | 69.7 | 1.40 | |
| [Cu(**13**)(**12**)]$^+$ | 3.12 | 439 | 68.9 | 0.94 | |
| [Cu(**13**)(**12**)]$^+$ | 2.58 | 430 | 68.4 | 0.76 | |

| | | | | | |
|---|---|---|---|---|---|
| 15 days after sealing the cells | | | | | |
| [Cu(**13**)(**7**)]$^{+}$ | 6.00 | 532 | 71.0 | 2.27 | 28.0 |
| [Cu(**13**)(**8**)]$^{+}$ | 5.99 | 530 | 71.8 | 2.28 | 28.1 |
| [Cu(**13**)(**9**)]$^{+}$ | 6.16 | 544 | 71.5 | 2.40 | 29.6 |
| [Cu(**13**)(**10**)]$^{+}$ | 5.36 | 518 | 70.8 | 1.96 | 24.2 |
| [Cu(**13**)(**11**)]$^{+}$ | 4.86 | 489 | 71.9 | 1.71 | 21.1 |
| [Cu(**13**)(**12**)]$^{+}$ | 2.67 | 448 | 70.4 | 0.84 | 10.4 |
| N719 | 16.98 | 674 | 70.9 | 8.11 | 100 |
| 22 days after sealing the cells | | | | | |
| [Cu(**13**)(**7**)]$^{+}$ | 5.94 | 536 | 70.3 | 2.23 | |
| [Cu(**13**)(**8**)]$^{+}$ | 5.97 | 532 | 71.6 | 2.27 | |
| [Cu(**13**)(**9**)]$^{+}$ | 6.31 | 541 | 71.0 | 2.42 | |
| [Cu(**13**)(**10**)]$^{+}$ | 5.47 | 522 | 70.6 | 2.02 | |
| [Cu(**13**)(**11**)]$^{+}$ | 4.99 | 487 | 71.3 | 1.73 | |
| [Cu(**13**)(**12**)]$^{+}$ | 2.77 | 466 | 70.2 | 0.91 | |
| | | | | | |

Table S3. DSC performance data for duplicate masked cells using anchoring ligand **13** and first-generation ancillary ligands, and $CH_2Cl_2$ in the $[CuL_2]^+$ dipping cycle. Relative efficiencies (last column) are with respect to 100% for standard dye N719 measured under the same conditions. $V_{OC}$ = open circuit voltage, $J_{SC}$ = short circuit current density, *ff* = fill factor.

| Anchored dye | $J_{sc}$ / mA cm$^{-2}$ | $V_{oc}$ / mV | *ff* / % | η / % | Rel. η / % |
|---|---|---|---|---|---|
| On the day of sealing the cell | | | | | |
| [Cu(**13**)(**1**)]$^+$ | 5.70 | 490 | 61.5 | 1.72 | 23.2 |
| [Cu(**13**)(**1**)]$^+$ | 5.47 | 490 | 69.4 | 1.86 | 25.1 |
| [Cu(**13**)(**2**)]$^+$ | 4.30 | 474 | 70.8 | 1.44 | 19.4 |
| [Cu(**13**)(**2**)]$^+$ | 4.65 | 475 | 69.8 | 1.54 | 20.8 |
| [Cu(**13**)(**3**)]$^+$ | 3.94 | 479 | 69.6 | 1.31 | 17.7 |
| [Cu(**13**)(**3**)]$^+$ | 4.05 | 469 | 67.9 | 1.29 | 17.4 |
| [Cu(**13**)(**4**)]$^+$ | 4.07 | 491 | 71.8 | 1.43 | 19.3 |
| [Cu(**13**)(**4**)]$^+$ | 3.02 | 496 | 71.9 | 1.08 | 14.6 |
| [Cu(**13**)(**5**)]$^+$ | 5.29 | 496 | 69.8 | 1.83 | 24.7 |
| [Cu(**13**)(**5**)]$^+$ | 5.35 | 492 | 70.4 | 1.85 | 25.0 |
| [Cu(**13**)(**6**)]$^+$ | 2.22 | 479 | 68.2 | 0.73 | 9.9 |
| [Cu(**13**)(**6**)]$^+$ | 2.94 | 485 | 68.3 | 0.97 | 13.1 |
| N719 | 16.31 | 637 | 71.3 | 7.41 | 100 |
| 1 day after sealing the cells | | | | | |
| [Cu(**13**)(**1**)]$^+$ | 5.09 | 488 | 65.8 | 1.63 | 21.1 |
| [Cu(**13**)(**1**)]$^+$ | 5.12 | 492 | 69.6 | 1.75 | 22.7 |
| [Cu(**13**)(**2**)]+ | 4.08 | 478 | 70.6 | 1.38 | 17.9 |
| [Cu(**13**)(**2**)]+ | 4.04 | 474 | 69.8 | 1.34 | 17.4 |
| [Cu(**13**)(**3**)]+ | 3.51 | 483 | 69.8 | 1.18 | 15.3 |
| [Cu(**13**)(**3**)]+ | 4.16 | 475 | 66.9 | 1.32 | 17.1 |
| [Cu(**13**)(**4**)]+ | 3.92 | 501 | 70.7 | 1.39 | 18.0 |
| [Cu(**13**)(**4**)]+ | 2.83 | 498 | 70.2 | 0.99 | 12.8 |
| [Cu(**13**)(**5**)]+ | 4.98 | 496 | 70.6 | 1.74 | 22.6 |
| [Cu(**13**)(**5**)]+ | 5.11 | 494 | 70.3 | 1.78 | 23.1 |
| [Cu(**13**)(**6**)]+ | 2.55 | 503 | 66.4 | 0.85 | 11.0 |
| [Cu(**13**)(**6**)]+ | 3.09 | 496 | 67.7 | 1.04 | 13.5 |
| N719 | 16.55 | 663 | 70.3 | 7.71 | 100 |
| 2 days after sealing the cells | | | | | |
| [Cu(**13**)(**1**)]+ | 5.18 | 495 | 66.0 | 1.70 | 21.4 |
| [Cu(**13**)(**1**)]+ | 4.98 | 493 | 70.0 | 1.72 | 21.7 |
| [Cu(**13**)(**2**)]+ | 4.41 | 493 | 70.2 | 1.52 | 19.1 |
| [Cu(**13**)(**2**)]+ | 4.27 | 485 | 69.3 | 1.43 | 18.0 |
| [Cu(**13**)(**3**)]+ | 3.55 | 488 | 69.0 | 1.20 | 15.1 |
| [Cu(**13**)(**3**)]+ | 4.07 | 475 | 67.5 | 1.30 | 16.4 |
| [Cu(**13**)(**4**)]+ | 3.78 | 500 | 70.6 | 1.34 | 16.9 |
| [Cu(**13**)(**4**)]+ | 2.92 | 515 | 70.3 | 1.06 | 13.4 |
| [Cu(**13**)(**5**)]+ | 5.02 | 520 | 70.4 | 1.84 | 23.2 |
| [Cu(**13**)(**5**)]+ | 5.36 | 508 | 70.5 | 1.92 | 24.2 |
| [Cu(**13**)(**6**)]+ | 2.68 | 514 | 66.9 | 0.92 | 11.6 |
| [Cu(**13**)(**6**)]+ | 2.93 | 500 | 67.7 | 0.99 | 12.5 |
| N719 | 16.47 | 680 | 70.9 | 7.94 | 100 |
| 8 days after sealing the cells | | | | | |
| [Cu(**13**)(**1**)]+ | 5.21 | 505 | 66.8 | 1.76 | 21.6 |
| [Cu(**13**)(**1**)]+ | 5.13 | 502 | 70.5 | 1.82 | 22.3 |
| [Cu(**13**)(**2**)]+ | 4.40 | 502 | 71.6 | 1.58 | 19.4 |
| [Cu(**13**)(**2**)]+ | 4.27 | 508 | 70.6 | 1.53 | 18.8 |
| [Cu(**13**)(**3**)]+ | 3.87 | 510 | 70.0 | 1.38 | 16.9 |

| | | | | | |
|---|---|---|---|---|---|
| [Cu(**13**)(**3**)]+ | 4.03 | 482 | 68.8 | 1.34 | 16.4 |
| [Cu(**13**)(**4**)]+ | 3.79 | 510 | 72.3 | 1.40 | 17.2 |
| [Cu(**13**)(**4**)]+ | 3.15 | 546 | 72.2 | 1.24 | 15.2 |
| [Cu(**13**)(**5**)]+ | 5.43 | 545 | 65.9 | 1.95 | 23.9 |
| [Cu(**13**)(**5**)]+ | 5.49 | 540 | 71.8 | 2.13 | 26.1 |
| [Cu(**13**)(**6**)]+ | 2.96 | 540 | 66.6 | 1.06 | 13.0 |
| [Cu(**13**)(**6**)]+ | 2.95 | 503 | 69.6 | 1.03 | 12.6 |
| N719 | 16.51 | 692 | 71.5 | 8.16 | 100 |
| 15 days after sealing the cells | | | | | |
| [Cu(**13**)(**1**)]+ | 4.99 | 498 | 67.1 | 1.67 | |
| [Cu(**13**)(**1**)]+ | 5.17 | 508 | 70.1 | 1.84 | |
| [Cu(**13**)(**2**)]+ | 4.41 | 503 | 71.0 | 1.57 | |
| [Cu(**13**)(**2**)]+ | 4.30 | 518 | 69.9 | 1.55 | |
| [Cu(**13**)(**3**)]+ | 3.97 | 525 | 70.2 | 1.46 | |
| [Cu(**13**)(**3**)]+ | 4.20 | 498 | 67.4 | 1.41 | |
| [Cu(**13**)(**4**)]+ | 3.77 | 526 | 72.7 | 1.44 | |
| [Cu(**13**)(**4**)]+ | 3.12 | 542 | 71.5 | 1.21 | |
| [Cu(**13**)(**5**)]+ | 5.59 | 550 | 65.7 | 2.02 | |
| [Cu(**13**)(**5**)]+ | 5.54 | 545 | 71.8 | 2.17 | |
| [Cu(**13**)(**6**)]+ | 2.87 | 537 | 67.3 | 1.04 | |
| [Cu(**13**)(**6**)]+ | 2.82 | 498 | 70.7 | 0.99 | |
| 24 days after sealing cells | | | | | |
| [Cu(**13**)(**1**)]+ | 4.67 | 485 | 68.0 | 1.54 | 19.4 |
| [Cu(**13**)(**1**)]+ | 4.86 | 494 | 69.4 | 1.67 | 21.1 |
| [Cu(**13**)(**2**)]+ | 4.16 | 494 | 71.1 | 1.46 | 18.4 |
| [Cu(**13**)(**2**)]+ | 4.51 | 518 | 67.6 | 1.58 | 19.9 |
| [Cu(**13**)(**3**)]+ | 4.20 | 525 | 67.6 | 1.49 | 18.8 |
| [Cu(**13**)(**3**)]+ | 4.72 | 508 | 62.6 | 1.50 | 18.9 |
| [Cu(**13**)(**4**)]+ | 3.94 | 532 | 71.6 | 1.50 | 18.9 |
| [Cu(**13**)(**4**)]+ | 3.19 | 539 | 70.7 | 1.22 | 15.4 |
| [Cu(**13**)(**5**)]+ | 5.32 | 541 | 68.0 | 1.95 | 24.6 |
| [Cu(**13**)(**5**)]+ | 5.45 | 537 | 70.5 | 2.06 | 26.0 |
| [Cu(**13**)(**6**)]+ | 2.93 | 535 | 66.2 | 1.04 | 13.1 |
| [Cu(**13**)(**6**)]+ | 3.19 | 521 | 69.1 | 1.15 | 14.5 |
| N719 | 15.86 | 698 | 71.6 | 7.92 | 100 |

Table S4. DSC performance data for duplicate masked cells using anchoring ligand **13** and second-generation ancillary ligands, and $CH_2Cl_2$ in the $[CuL_2]^+$ dipping cycle. Relative efficiencies (last column) are with respect to 100% for standard dye N719 measured under the same conditions. $V_{OC}$ = open circuit voltage, $J_{SC}$ = short circuit current density, *ff* = fill factor.

| Anchored dye | $J_{sc}$ / mA cm$^{-2}$ | $V_{oc}$ / mV | *ff* / % | η / % | Rel. η / % |
|---|---|---|---|---|---|
| On day of sealing the cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 4.97 | 491 | 61.1 | 1.49 | 20.1 |
| [Cu(**13**)(**7**)]$^+$ | 4.32 | 509 | 68.1 | 1.50 | 20.3 |
| [Cu(**13**)(**8**)]$^+$ | 4.08 | 469 | 67.9 | 1.30 | 17.6 |
| [Cu(**13**)(**8**)]$^+$ | 3.86 | 467 | 69.7 | 1.26 | 17.0 |
| [Cu(**13**)(**9**)]$^+$ | 2.50 | 426 | 66.4 | 0.71 | 9.6 |
| [Cu(**13**)(**9**)]$^+$ | 2.60 | 428 | 65.3 | 0.73 | 9.9 |
| [Cu(**13**)(**10**)]$^+$ | 2.73 | 459 | 68.5 | 0.86 | 11.6 |
| [Cu(**13**)(**10**)]$^+$ | 2.65 | 455 | 66.3 | 0.80 | 10.8 |
| [Cu(**13**)(**11**)]$^+$ | 1.62 | 414 | 65.5 | 0.44 | 5.9 |
| [Cu(**13**)(**11**)]$^+$ | 1.78 | 418 | 67.2 | 0.50 | 6.8 |
| [Cu(**13**)(**12**)]$^+$ | 1.29 | 413 | 63.3 | 0.34 | 4.6 |
| [Cu(**13**)(**12**)]$^+$ | 1.63 | 411 | 61.1 | 0.41 | 5.5 |
| N719 | 16.44 | 647 | 69.5 | 7.40 | 100 |
| 1 day after sealing cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 5.07 | 532 | 68.3 | 1.84 | 22.7 |
| [Cu(**13**)(**7**)]$^+$ | 4.27 | 532 | 69.6 | 1.58 | 19.5 |
| [Cu(**13**)(**8**)]$^+$ | 4.64 | 505 | 69.6 | 1.63 | 20.1 |
| [Cu(**13**)(**8**)]$^+$ | 4.35 | 495 | 70.8 | 1.52 | 18.7 |
| [Cu(**13**)(**9**)]$^+$ | 3.25 | 454 | 69.2 | 1.02 | 12.6 |
| [Cu(**13**)(**9**)]$^+$ | 3.10 | 456 | 68.6 | 0.97 | 12.1 |
| [Cu(**13**)(**10**)]$^+$ | 3.09 | 479 | 69.7 | 1.03 | 12.7 |
| [Cu(**13**)(**10**)]$^+$ | 3.12 | 485 | 66.5 | 1.01 | 12.5 |
| [Cu(**13**)(**11**)]$^+$ | 2.08 | 449 | 69.1 | 0.64 | 7.9 |
| [Cu(**13**)(**11**)]$^+$ | 2.31 | 440 | 69.0 | 0.70 | 8.6 |
| [Cu(**13**)(**12**)]$^+$ | 1.57 | 436 | 67.6 | 0.46 | 5.7 |
| [Cu(**13**)(**12**)]$^+$ | 2.08 | 431 | 46.7 | 0.42 | 5.2 |
| N719 | 17.02 | 681 | 70.0 | 8.11 | 100 |
| 2 days after sealing cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 4.96 | 529 | 69.3 | 1.82 | 23.2 |
| [Cu(**13**)(**7**)]$^+$ | 4.24 | 531 | 69.9 | 1.57 | 20.0 |
| [Cu(**13**)(**8**)]$^+$ | 4.42 | 496 | 69.2 | 1.52 | 19.3 |
| [Cu(**13**)(**8**)]$^+$ | 4.22 | 494 | 71.0 | 1.48 | 18.8 |
| [Cu(**13**)(**9**)]$^+$ | 3.16 | 455 | 69.6 | 1.00 | 12.7 |
| [Cu(**13**)(**9**)]$^+$ | 3.04 | 458 | 68.1 | 0.95 | 12.1 |
| [Cu(**13**)(**10**)]$^+$ | 3.23 | 490 | 69.6 | 1.10 | 14.0 |
| [Cu(**13**)(**10**)]$^+$ | 3.17 | 488 | 66.9 | 1.03 | 13.1 |
| [Cu(**13**)(**11**)]$^+$ | 2.17 | 451 | 68.9 | 0.67 | 8.5 |
| [Cu(**13**)(**11**)]$^+$ | 2.30 | 438 | 68.7 | 0.69 | 8.8 |
| [Cu(**13**)(**12**)]$^+$ | 1.65 | 440 | 67.9 | 0.49 | 6.2 |
| [Cu(**13**)(**12**)]$^+$ | 2.30 | 432 | 45.2 | 0.45 | 5.7 |
| N719 | 16.59 | 673 | 70.4 | 7.86 | 100 |
| 8 days after sealing cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 4.92 | 541 | 69.7 | 1.85 | |
| [Cu(**13**)(**7**)]$^+$ | 3.89 | 565 | 69.6 | 1.53 | |
| [Cu(**13**)(**8**)]$^+$ | 4.47 | 505 | 70.3 | 1.59 | |
| [Cu(**13**)(**8**)]$^+$ | 4.26 | 522 | 71.0 | 1.58 | |

| | | | | | |
|---|---|---|---|---|---|
| [Cu(**13**)(**9**)]$^+$ | 3.29 | 467 | 70.6 | 1.09 | |
| [Cu(**13**)(**9**)]$^+$ | 3.26 | 489 | 69.8 | 1.11 | |
| [Cu(**13**)(**10**)]$^+$ | 3.39 | 514 | 69.8 | 1.22 | |
| [Cu(**13**)(**10**)]$^+$ | 3.20 | 493 | 67.4 | 1.06 | |
| [Cu(**13**)(**11**)]$^+$ | 2.20 | 454 | 69.6 | 0.69 | |
| [Cu(**13**)(**11**)]$^+$ | 2.50 | 446 | 69.4 | 0.77 | |
| [Cu(**13**)(**12**)]$^+$ | 1.66 | 440 | 68.4 | 0.50 | |
| [Cu(**13**)(**12**)]$^+$ | 2.54 | 444 | 44.4 | 0.50 | |
| 15 days after sealing the cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 5.09 | 551 | 69.6 | 1.95 | 25.3 |
| [Cu(**13**)(**7**)]$^+$ | 3.94 | 568 | 69.0 | 1.54 | 20.0 |
| [Cu(**13**)(**8**)]$^+$ | 4.49 | 509 | 70.3 | 1.61 | 20.9 |
| [Cu(**13**)(**8**)]$^+$ | 4.69 | 537 | 70.3 | 1.77 | 23.0 |
| [Cu(**13**)(**9**)]$^+$ | 3.44 | 471 | 70.4 | 1.14 | 14.8 |
| [Cu(**13**)(**9**)]$^+$ | 3.59 | 497 | 68.9 | 1.23 | 16.0 |
| [Cu(**13**)(**10**)]$^+$ | 3.58 | 523 | 69.1 | 1.29 | 16.7 |
| [Cu(**13**)(**10**)]$^+$ | 3.40 | 499 | 66.7 | 1.13 | 14.7 |
| [Cu(**13**)(**11**)]$^+$ | 2.34 | 459 | 69.4 | 0.75 | 9.7 |
| [Cu(**13**)(**11**)]$^+$ | 2.68 | 449 | 68.7 | 0.83 | 10.8 |
| [Cu(**13**)(**12**)]$^+$ | 1.87 | 459 | 69.8 | 0.60 | 7.8 |
| [Cu(**13**)(**12**)]$^+$ | 2.68 | 440 | 42.8 | 0.51 | 6.6 |
| N719 | 16.02 | 691 | 69.6 | 7.71 | 100 |
| 22 days after sealing the cells | | | | | |
| [Cu(**13**)(**7**)]$^+$ | 5.17 | 561 | 69.4 | 2.01 | 25.3 |
| [Cu(**13**)(**7**)]$^+$ | 4.03 | 573 | 68.1 | 1.57 | 19.8 |
| [Cu(**13**)(**8**)]$^+$ | 4.54 | 512 | 70.0 | 1.63 | 20.5 |
| [Cu(**13**)(**8**)]$^+$ | 4.77 | 536 | 69.2 | 1.77 | 22.3 |
| [Cu(**13**)(**9**)]$^+$ | 3.54 | 469 | 70.5 | 1.17 | 14.7 |
| [Cu(**13**)(**9**)]$^+$ | 3.43 | 484 | 70.1 | 1.16 | 14.6 |
| [Cu(**13**)(**10**)]$^+$ | 3.71 | 522 | 68.1 | 1.32 | 16.6 |
| [Cu(**13**)(**10**)]$^+$ | 3.48 | 491 | 66.2 | 1.13 | 14.2 |
| [Cu(**13**)(**11**)]$^+$ | 2.43 | 462 | 69.3 | 0.78 | 9.8 |
| [Cu(**13**)(**11**)]$^+$ | 2.83 | 449 | 69.1 | 0.88 | 11.1 |
| [Cu(**13**)(**12**)]$^+$ | 2.03 | 463 | 69.2 | 0.65 | 8.2 |
| [Cu(**13**)(**12**)]$^+$ | 3.01 | 449 | 31.9 | 0.43 | 5.4 |
| N719 | 16.16 | 709 | 69.3 | 7.94 | 100 |

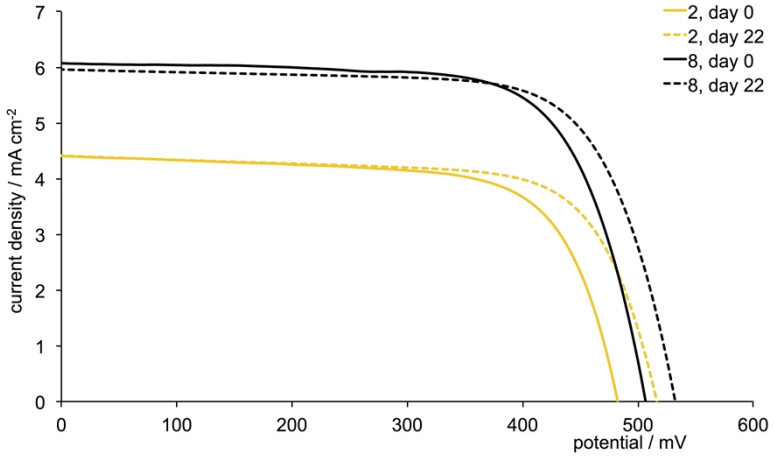



Fig. S1. J–V curves for dyes [Cu(**13**)(**2**)]$^+$ and [Cu(**13**)(**8**)]$^+$ (n-butyl substituents) on day of sealing the DSC (day 0) and after 22 days showing enhancement of $J_{SC}$ with second-generation ligand. Dye assembly was from an acetone solution of the homolpetic complex.

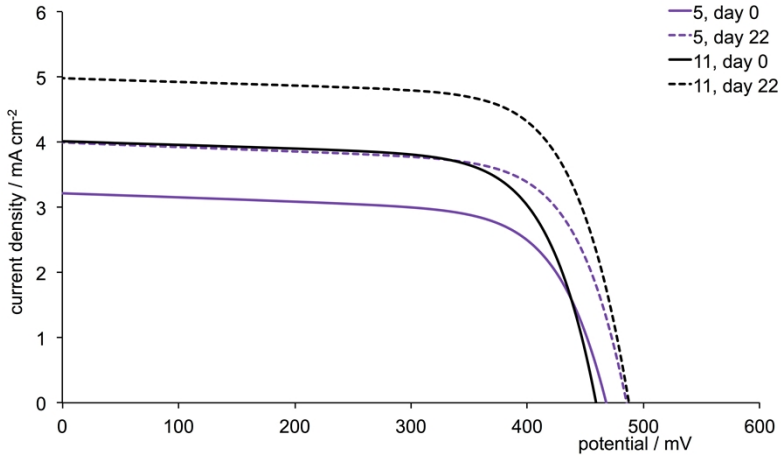



Fig. S2. J–V curves for dyes [Cu(**13**)(**5**)]$^+$ and [Cu(**13**)(**11**)]$^+$ (phenyl substituents) on day of sealing the DSC (day 0) and after 22 days. Dye assembly was from an acetone solution of the homolpetic complex.

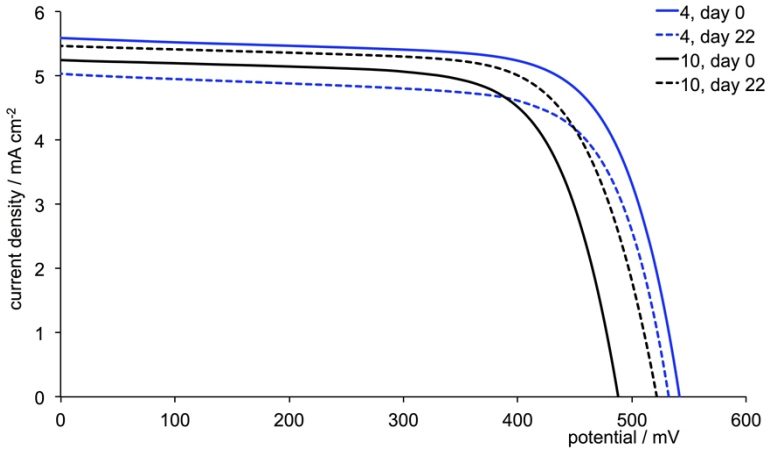



Fig. S3. J–V curves for dyes [Cu(**13**)(**4**)]$^+$ and [Cu(**13**)(**10**)]$^+$ (n-hexyl substituents) on day of sealing the DSC (day 0) and after 22 days. Dye assembly was from an acetone solution of the homolpetic complex.

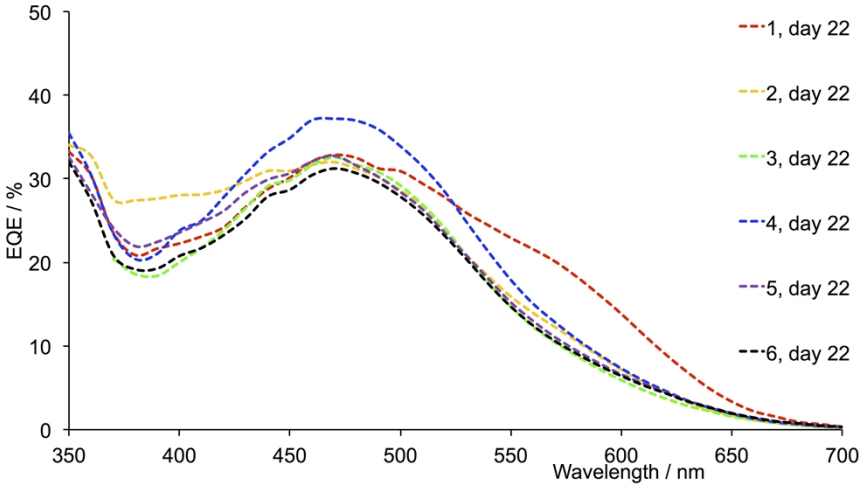



Fig. S4. EQE spectra of the DSCs (22 days after sealing) with dyes containing ancillary ligands **1–6**. Dye assembly was from an acetone solution of the homolpetic complex.

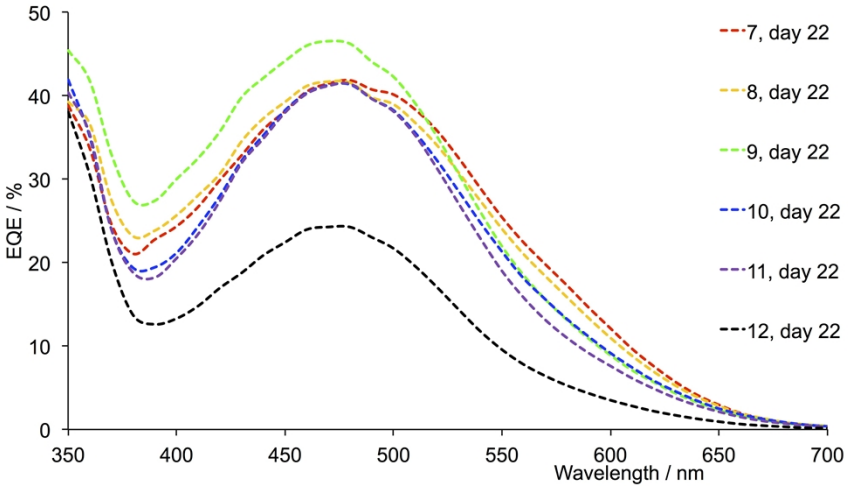



Fig. S5. EQE spectra of the DSCs (22 days after sealing) with dyes containing ancillary ligands **7–12**. Dye assembly was from an acetone solution of the homolpetic complex.

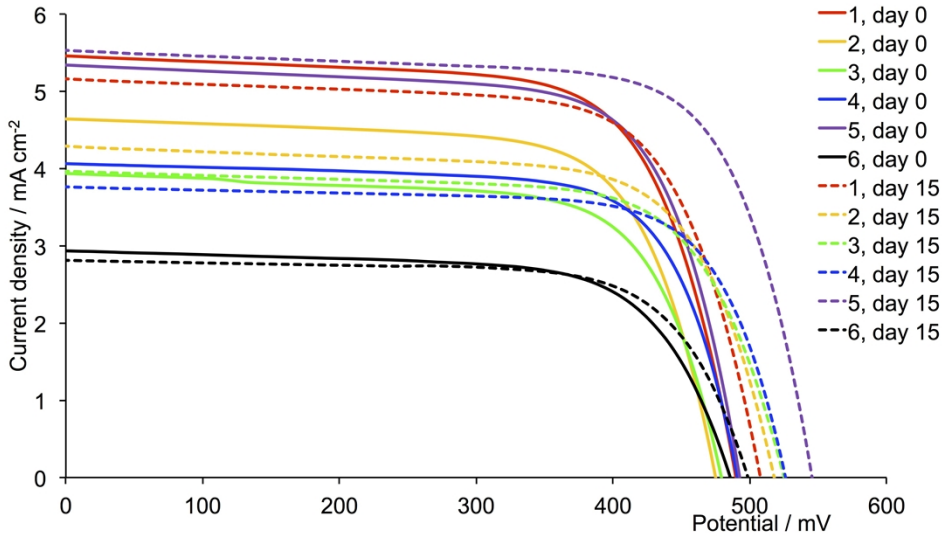



Fig. S6 J–V curves for dyes [Cu(**13**)(L)]$^+$ with L = **1**–**6** on day of sealing the DSCs (day 0) and after 15 days showing improvement of $V_{OC}$. $CH_2Cl_2$ was used in the $[CuL_2]^+$ dipping cycle.

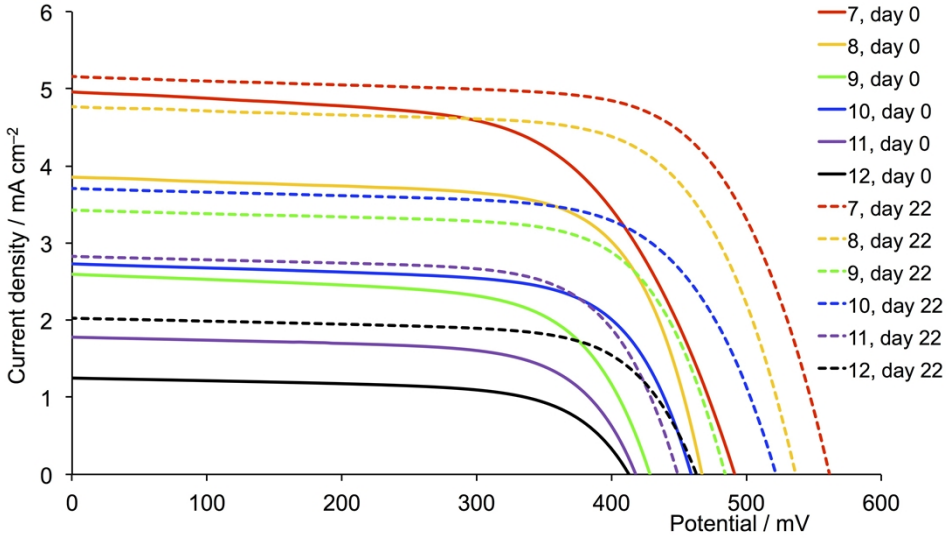



Fig. S7 J–V curves for dyes [Cu(**13**)(L)]$^+$ with L = **7**–**12** on day of sealing the DSCs (day 0) and after 22 days showing improvement both in $V_{OC}$ and $J_{SC}$ with aging. $CH_2Cl_2$ was used in the $[CuL_2]^+$ dipping cycle.

## References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2 B. Bozic-Weber, S. Y. Brauchli, E. C. Constable, S. O. Fürer, C. E. Housecroft, F. J. Malzner, I. A. Wright and J. A. Zampese, *Dalton Trans.*, 20**13**, **42**, 12293.