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SUPPLEMENTARY MATERIAL TO

Ligands containing 7-azaindole functionality for inner-sphere hydrogen bonding: Structural and photophysical investigations

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ANALYTICAL AND SPECTRAL DATA

7-Azaindole-3-carboxaldehyde 2-pyridylhydrazone ***(1)****.* Mp 260 °C (decomp.); δ_H (400 MHz; DMSO-d_6) 11.90 (s, 1H, H11), 10.54 (s, 1H, H6), 8.54 (d, 1H, *J* = 7.9 Hz, H1), 8.30 (d, 1H, *J* = 4.8 Hz, H3), 8.21 (s, 1H, H4), 8.08 (d, 1H, *J* = 4.9 Hz, H10), 7.80 (s, 1H, H5), 7.65 (t, 1H, *J* = 7.8 Hz, H8), 7.34 – 7.12 (m, 2H, H2 + H7), 6.70 (dd, 1H, *J* = 7.0, 4.9 Hz, H9), δ_C (100 MHz; DMSO-d_6) 157.4, 149.3, 147.8, 143.7, 137.9, 136.4, 129.8, 128.2, 116.6, 116.5, 114.0, 111.4, 105.7; ν_{max} (ATR, cm^{-1}) 3205m br, 3068m, 2979m, 2784w, 2627w, 1598s, 1578s, 1541m, 1499w, 1456m sh, 1439s, 1413m, 1317m, 1286s, 1241m, 1126s, 1083s, 991s, 920m, 812w, 792w, 760s, 726m, 623s; λ_{max}(DMSO) /nm (ε /L mol^{-1} cm^{-1}) 326 (26700). Single crystals for SCXRD were prepared by recrystallization from ethanol.

*7-Azaindole-3-carboxaldehyde 4-(*N*-imidazolyl)phenyl imine* ***(2)****.* Mp 270 °C (decomp.); δ_H (400 MHz; DMSO-d_6) 12.34 (1H, br s, H11), 8.75 (s, 1H, H5), 8.67 (d, 1H, *J* = 7.8 Hz, H1), 8.35 (d, 1H, *J* = 4.7 Hz, H3), 8.26 (s, 1H, H4), 8.17 (s, 1H, H8), 7.75 (s, 1H, H10), 7.67 (d, 2H, *J* = 8.3 Hz, H6), 7.38 (d, 2H, *J* = 8.2 Hz, H7), 7.26 (dd, 1H, *J* = 7.8, 4.7 Hz, H2), 7.11 (s, 1H, H9) δ_C (100 MHz; DMSO-d_6) 155.7, 151.3, 149.5, 144.3, 135.5, 134.0, 133.9, 130.1, 129.8, 122.0, 121.2, 118.1, 117.4, 117.1, 113.7; ν_{max} (ATR, cm^{-1}) 3210w br, 3111m, 3070m, 3019m, 2808m, 2597w, 1620m, 1607m, 1575s, 1505m, 1465m, 1416s, 1280s, 1243s, 1134s, 1116s, 1054s, 960w, 896m, 842s, 804s, 766s, 657s, 626s; λ_{max} (DMSO) /nm (ε /L mol^{-1} cm^{-1}) 331 (24100). Single crystals for SCXRD were prepared by recrystallization from ethanol.

*3-(4-(*N*-Imidazolyl)phenyl)aminomethyl-7-azaindole* ***(3)****.* Mp 234-238 °C; δ_H (400 MHz; DMSO-d_6) 11.44 (s, 1H, H12), 8.19 (d, 1H, *J* = 4.2 Hz, H1), 8.06 (d, 1H, *J* = 7.8 Hz, H3), 7.95 (s, 1H, H9), 7.50 – 7.44 (m, 2H, H4 + H11), 7.25 (d, 2H, *J* = 8.5 Hz, H8), 7.04 (dd, 1H, *J* = 7.8, 4.6 Hz, H2), 7.00 (s, 1H, H10), 6.75 (d, 2H, *J* = 8.7 Hz, H7), 6.25 (t, 1H, *J* = 5.5 Hz, H6), 4.40 (d, 2H, *J* = 5.6 Hz, H5) δ_C (100 MHz; DMSO-d_6) 148.7, 148.0, 142.6, 135.4, 129.1, 127.1, 126.2, 124.2, 121.9, 118.9, 118.4, 115.0, 112.6, 111.4, 38.7; ν_{max} (ATR, cm^{-1}) 3247 m br, 3122m, 3092w, 3031m, 2886w, 1610s, 1582m, 1534s, 1519s, 1496m, 1457m, 1418s, 1359w, 1330s, 1306m, 1292m, 1275w, 1244m, 1180w, 1119s, 1058s, 982w, 961w, 911w, 842w, 817s, 765s, 659s; λ_{max} (DMSO) /nm (ε /L mol^{-1} cm^{-1}) 277 (25600). Single crystals for SCXRD were prepared by recrystallization from ethanol.

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*Poly-[Cu(**1**)Cl$_2$]*. Mp 196-198 °C (decomp.); Found C, 41.62; H, 3.04; N, 18.21; Calculated for [Cu(**1**)Cl$_2$] ($C_{13}H_{11}N_5CuCl_2$) C, 42.01; H, 2.98; N, 18.84%; ν_{max} (ATR, cm^{-1}) 3450 w br, 3229m br, 3104m, 1616s, 1569m, 1520m, 1502s, 1484s, 1427s, 1409s, 1337w, 1306m, 1248m, 1152w, 1119s, 1091s, 1059s, 1039m, 1014m, 937w, 869w, 826w, 793w, 767s sh, 692m, 622s. Phase purity was confirmed with X-ray powder diffraction.

X-RAY CRYSTALLOGRAPHY

All crystal and diffraction data are given in Table S-I. Single crystal X-ray diffraction data were recorded using a Bruker D8 Quest ECO diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.71073 Å) and a Photon II C14 pixel array detector. Temperature control was provided with an Oxford Cryosystems Cryostream 800. Crystals were mounted on Mitegen micromounts in NVH immersion oil, and datasets were collected using ϕ and ω scans. Data collection and reduction was controlled with the Bruker APEX-3 suite of programs,[1] and multi-scan absorption corrections were applied using SADABS.[2] The corrected intensity data were solved using the intrinsic phasing routine in SHELXT,[3] and structural models were refined on F^2 with full matrix least-squares procedures in SHELXL,[4] operating within the OLEX-2 GUI.[5] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were modelled as isotropic and placed in calculated positions, except for those involved in hydrogen bonding which were located from Fourier residuals and refined with distance restraints and U_{iso} dependencies 1.2 or 1.5 times those their carrier atoms. CCDC 2269543-2269546.

Table 1 Crystal and refinement parameters for all structures

Identification code	1	2	3	*poly*-[Cu(**1**)Cl_2]
Empirical formula	$C_{13}H_{11}N_5$	$C_{17}H_{13}N_5$	$C_{17}H_{15}N_5$	$C_{13}H_{11}Cl_2CuN_5$
Formula weight	237.27	287.32	289.34	371.71
Temperature/K	166	150	150	150
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a/Å	17.0143(11)	5.8887(7)	6.1005(3)	7.8301(4)
b/Å	17.1117(10)	8.0233(10)	25.2741(12)	13.5294(6)
c/Å	7.9866(6)	28.779(3)	9.7148(5)	13.7427(6)
α/°	90	90	90	90
β/°	93.538(2)	94.406(3)	104.095(2)	90
γ/°	90	90	90	90
Volume/Å^3	2320.8(3)	1355.7(3)	1452.78(12)	1455.85(12)
Z	8	4	4	4
ρ_{calc}g/cm^3	1.358	1.408	1.323	1.696
2Θ range /°	5.638 to 51.996	5.678 to 51.436	4.614 to 52.946	5.928 to 54.99
Index ranges	$-20 \le h \le 20$, $-20 \le k \le 21$, $-9 \le l \le 9$	$-7 \le h \le 7$, $-9 \le k \le 9$, $-35 \le l \le 35$	$-7 \le h \le 7$, $-31 \le k \le 31$, $-12 \le l \le 10$	$-10 \le h \le 10$, $-17 \le k \le 17$, $-17 \le l \le 14$
Reflections collected	30794	17657	17760	19212
Independent reflections	4542 [R_{int} = 0.0761, R_{sigma} = 0.0513]	2579 [R_{int} = 0.1358, R_{sigma} = 0.0951]	2994 [R_{int} = 0.0574, R_{sigma} = 0.0454]	3346 [R_{int} = 0.0575, R_{sigma} = 0.0467]
Data/restraints/parameters	4542/4/337	2579/1/202	2994/2/205	3346/2/196
Goodness-of-fit on F^2	1.037	1.047	1.06	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1309	R_1 = 0.0752, wR_2 = 0.1306	R_1 = 0.0494, wR_2 = 0.0973	R_1 = 0.0327, wR_2 = 0.0663
Final R indexes [all data]	R_1 = 0.0981, wR_2 = 0.1524	R_1 = 0.1424, wR_2 = 0.1529	R_1 = 0.0812, wR_2 = 0.1095	R_1 = 0.0453, wR_2 = 0.0705
Largest peak/hole / e Å^{-3}	0.27/-0.25	0.22/-0.30	0.18/-0.24	0.53/-0.32
Flack Parameter	n/a	n/a	n/a	0.015(9)

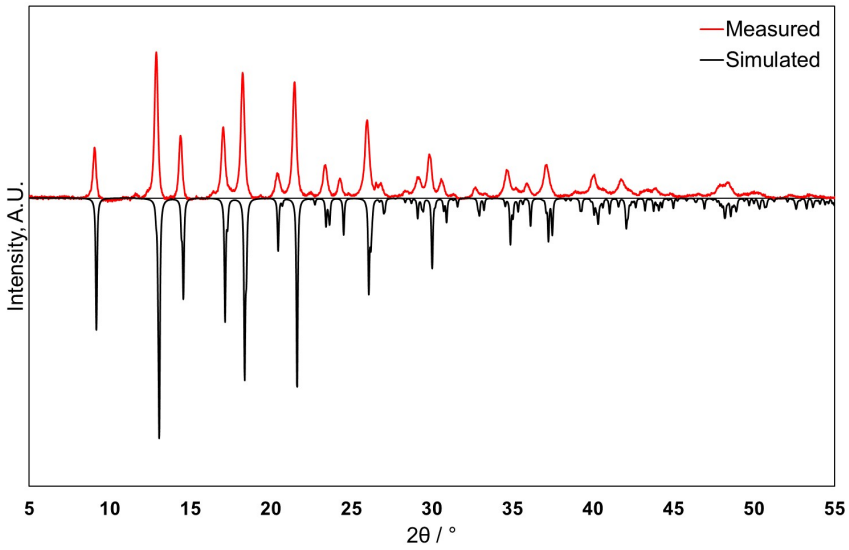

Figure S-1. X-ray powder diffraction pattern for *poly*-[Cu(**1**)Cl_2] comparing the measured data at room temperature (red) to the pattern simulated from the single crystal dataset (black, 150 K).

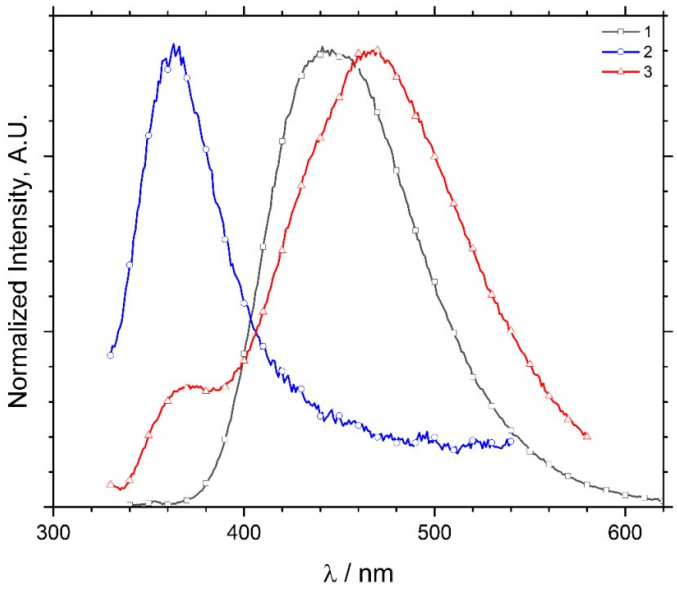

Figure S-2. Normalized emission spectra for compounds **1** (black, 27 μM, λ_{ex} = 318 nm), **2** (blue, 22 μM, λ_{ex} = 286 nm) and **3** (red, 26 μM, λ_{ex} = 300 nm) in MeCN.

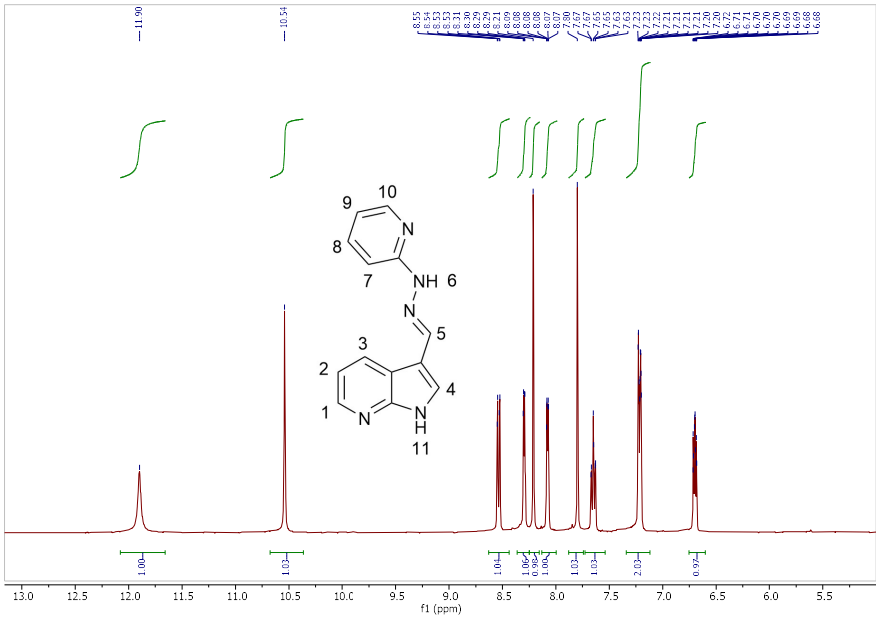

Figure S-3. ^{1}H NMR spectrum (d_6-DMSO, 400 MHz) for compound **1** with proton numbering scheme.

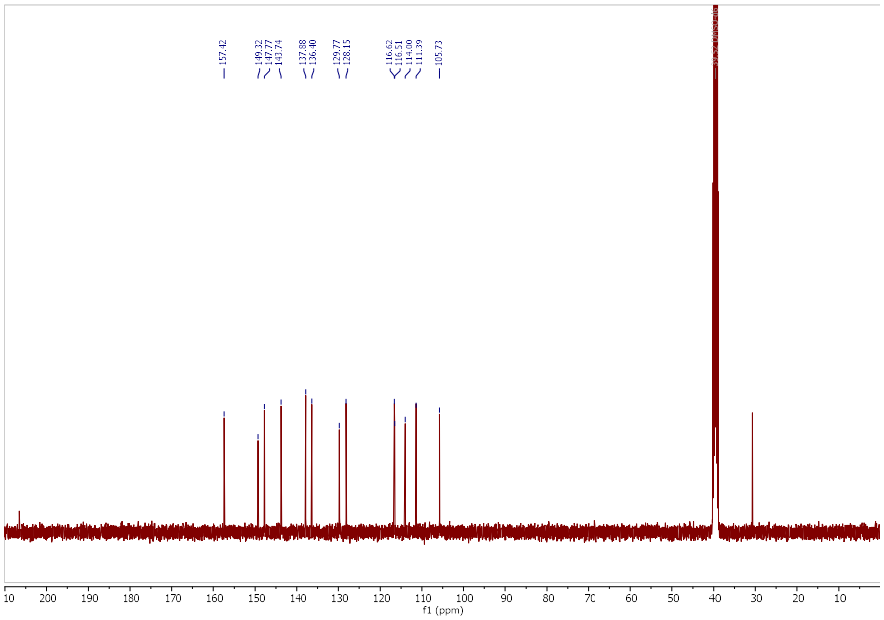

Figure S-4. ^{13}C NMR spectrum (d_6-DMSO, 100 MHz) for compound **1**.

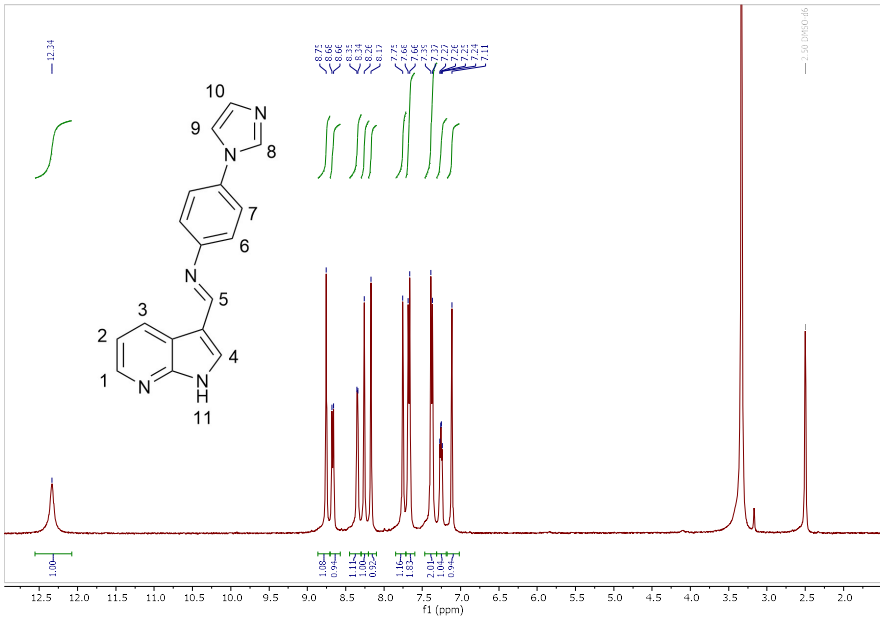

Figure S-5. ^{1}H NMR spectrum (d_6-DMSO, 400 MHz) for compound **2** with proton numbering scheme.

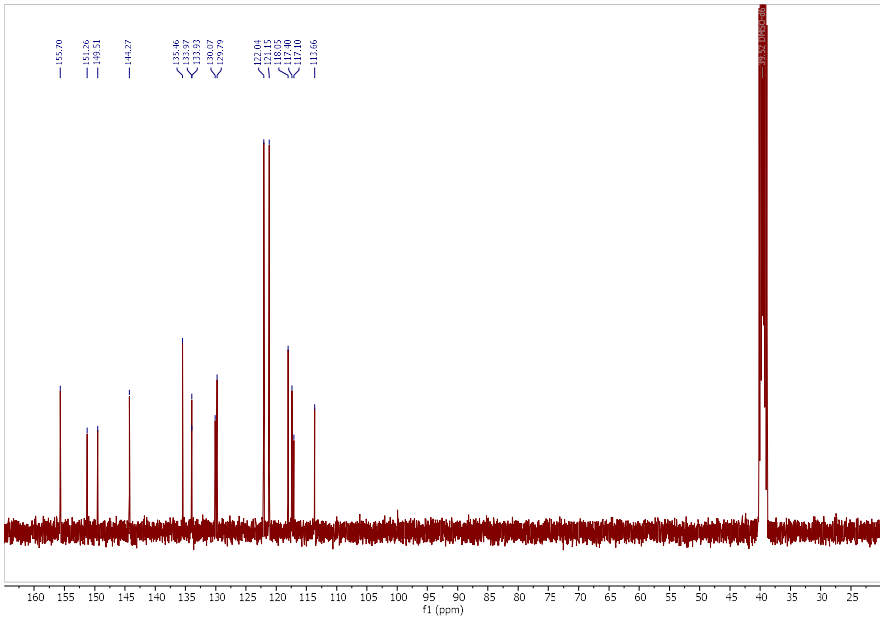

Figure S-6. ^{13}C NMR spectrum (d_6-DMSO, 100 MHz) for compound **2**.

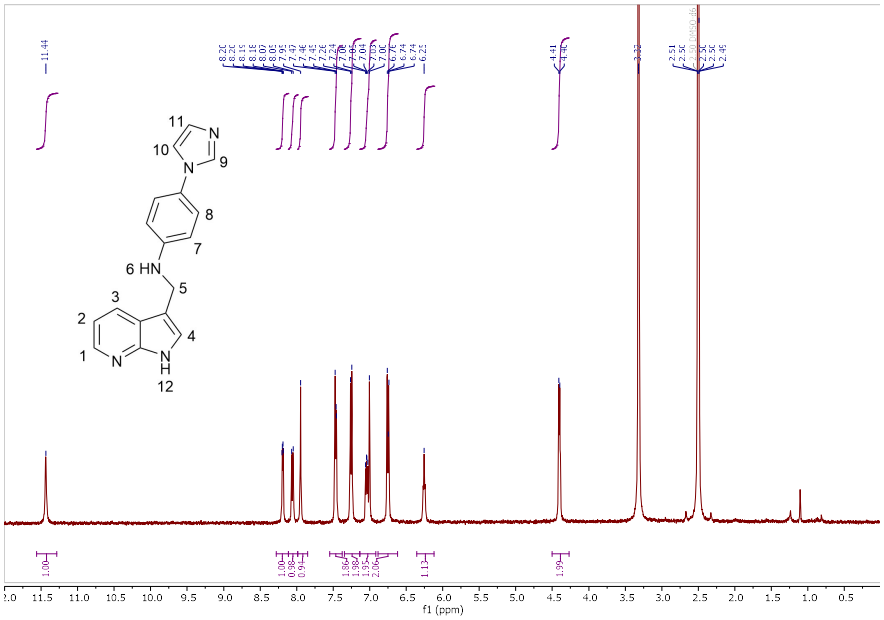

Figure S-7. ^{1}H NMR spectrum (d_6-DMSO, 400 MHz) for compound **3** with proton numbering scheme.

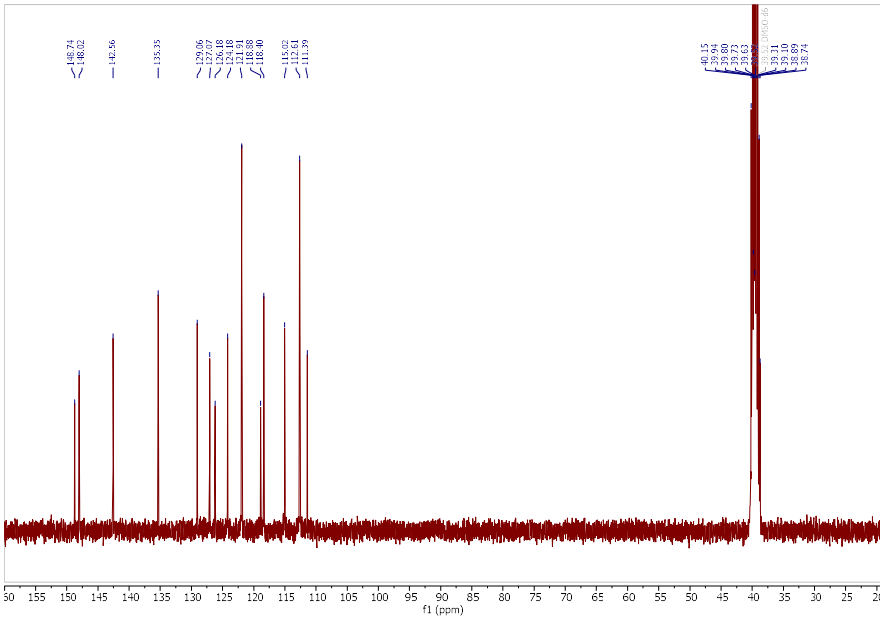

Figure S-8. ^{13}C NMR spectrum (d_6-DMSO, 100 MHz) for compound **3**.

REFERENCES

1. Bruker-AXS *APEX-3,* Bruker-AXS Inc., Madison, WI, 2018
2. Bruker-AXS *SADABS 2016/2,* Bruker-AXS Inc., Madison, WI, 2016
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