Electronic Supplementary Information

A C(π-hole)···Cl-Zn tetrel interaction driving a metal-organic supramolecular assembly

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1. Experimental Section

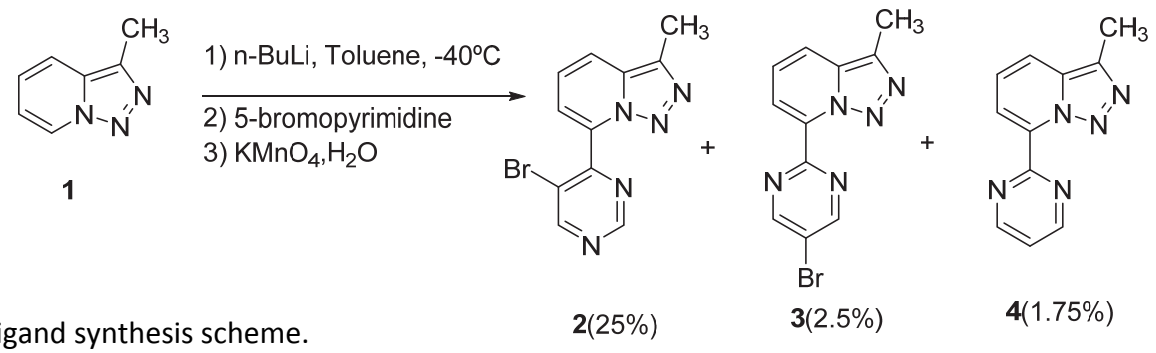
1.1 General procedures

Starting materials, if commercially available, were purchased and used as such, provided that suitable checks (melting ranges, refractive indices and gas chromatography) had confirmed the claimed purity. When known compounds had to be prepared by literature procedures, pertinent references are given. Air- and moisture-sensitive materials were stored in Schlenk tubes. They were protected by and handled under argon, in appropriate glassware. Tetrahydrofuran was dried by distillation from sodium after the characteristic blue colour of sodium diphenyl ketyl. Melting points or ranges (m.p.) given were determined on a Kofler heated stage and found to be reproducible after recrystallization. Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 63–210 µm). ^{1}H and (^{1}H decoupled) ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 400 or 300 and 101 or 75 MHz, respectively. Chemical shifts are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (δ = 7.27 ppm). Coupling constants (J) are given in Hz. Coupling patterns are abbreviated as, for example, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sp (septuplet), td (triplet of doublets), m (multiplet), app. s (apparent singlet) and br. (broad). COSY experiments were performed for all compounds. HRMS were recorded using a AB SCIEX Triple TOF TOF electrospray ionization (ESI positive) instrument.IR

spectra were recorded using a Thermo Nicolet iS10 FT-IR ATR. UV-Vis absorption spectra were recorded on an Agilent 8453 spectroscopy system. The emission spectra were recorded with a PTI MO-5020 spectrofluorimeter in the 300–500 nm range. The solvents used were of spectroscopic or equivalent grade. Water was twice distilled and passed through a Millipore apparatus.

7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (bptpy, 1)

At -40°C, butyllithium (1.9 mL) in hexane (1.3M) was added dropwise to a stirred solution of 3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (0.3 g, 2.25 mmol 1 eq) in toluene (165 mL).[1] After 30 minutes a solution of 5-bromopyrimidine (1.11 g, 6.75 mmol, 3eq) in toluene (10 mL) was added dropwise to the reaction mixture, and was allowed to react during 2 hours. Then the solution was allowed to reach room temperature and a solution of $KMnO_4$ (0.4 g, 2.48 mmol, 1.1 eq) in 100 mL of water was added, as well as 50 mL of saturated aqueous solution of ammonium chloride. After 30 minutes the organic layer was separated and the aqueous layer extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over sodium sulfate, filtered, and evaporated. By ethyl acetate treatment a yellow solid (126 mg) was obtained and identified as 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine **1**. The filtrate was purified by cromatrotron eluting with hexane ethyl acetate to obtain: The starting material 3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (40 mg), 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (**1)** (36 mg) and, as secondary compounds, 7-(5-bromopyrimidin-2-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (**3)** (16 mg) and 3-methyl-7-(pyrimidin-2-yl)-[1,2,3]triazolo[1,5-*a*] pyridine (**4)** (9.5 mg). Mp: 207-210°C(AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.32 (s, 1H), 9.06 (s, 1H), 7.80 (dd, J = 8.9, 1.2Hz, 1H), 7.33 (dd, J = 8.9, 6.8Hz, 1H), 7.12 (dd, J = 6.8, 1.2Hz, 1H), 2.68 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4 (CH), 158.1 (C), 157.2 (CH), 135.5 (C), 133.2 (C), 132.0 (C), 123.4 (CH), 121.9 (C), 119.2 (CH), 116.9 (CH), 10.6 (CH3). MS (EI): m/z(%) = 291 (27), 288 (27), 260 (100), 236 (21), 234 (27), 182 (68), 156 (41), 129 (10), 76 (4). HRMS for $C_{11}H_8BrN_5$: 288.9963, found: 288.9956. IR (neat, cm^{-1}): 3262, 1554, 1510, 1426, 1343, 1138, 1019, 791, 777, 735, 666.



Ligand synthesis scheme.

[(ZnCl₂)₂(μ-bptpy)₂] (2)

To a solution of 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (**2)** (100 mg, 0.35 mmol) in dichloromethane (2 mL) was added with stirring $ZnCl_2.OEt_2$ (0.35 mL, 1M in ether).The solution was heated at 35ºC during 15 min. The white solid formed was crystallized in EtOH to obtain colorless crystals (14 mg).

2. Crystal structure description of 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (1)

The 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (bptpy) crystal structure exhibits standard bond lengths and angles (Fig S1). The pyrimidine and the triazolopyridine mean planes present an angle of 60.7°.

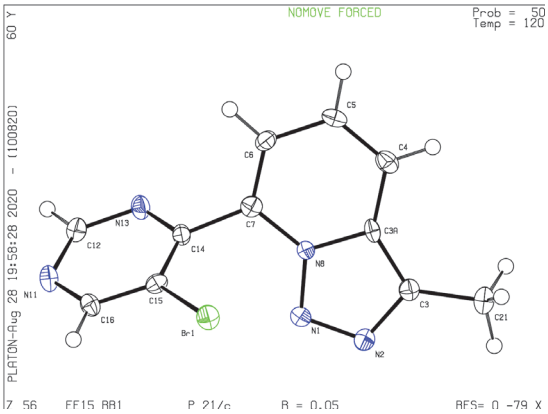


Figure S1. Thermal ellipsoid plot (50% probability level) for bptpy (**1**).

In the crystal structure, the bptpy molecules are linked through intermolecular C(sp^2)–H···Br interactions involving a pyrimidine C-H bond, thus, generating linear chains parallel to the *a* axis (Table S1). C-Br···N contacts are also present within the chains (Br···N distance of 3.444(1) Å, close to the sum of Van der Waals radii).[2] Chain assembly forms a double-strand structure through C(sp^3)-H···π and π···π triazolopyridine interactions (Fig. S2). The pyridine centroid···centroid (Cg···Cg)

distance is 3.67 Å, the Cg···plane distance is 3.37 Å and γ is 23.3º, being γ the angle between the centroid···centroid vector and the perpendicular to the pyridine mean plane. These double-chains pack together into a 3D array driven by a combination of C(sp^2)-H···N interactions. (Table S1, Fig. S3). The shortest Br ··· Br distance is 4.080(2)Å, clearly greater than the sum of Van der Waals radii.

Table S1. H-bonds (D-H···A) and contacts (D···A) lengths (Å) and angles (º) involved in the crystal packing of bptpy (**1**)

D-H···A	H···A	D···A	D-H···A	Symm. codes
C12-H12···Br1^{i}	2.94	3.513(4)	120.3	i: *-1+x, y, z*
C12-H12···N1^{ii}	2.53	3.392(5)	150.9	ii: *-x, 1/2+y, 3/2-z*
C16-H16···N2^{iii}	2.63	3.478(5)	149.1	iii: *1-x, 1/2+y, 3/2-z*
C21-H21A···Cg^{iii}	2.69	3.602	155.10	*-x, 1-y, 1-z*

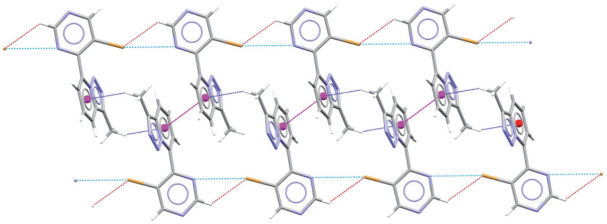


Figure S2. Chain structure of bptpy along the [100] direction generated by C-H···Br interactions (orange dashed lines), Br···N contacts, (cyan dashed lines), C-H···π (blue dashed lines) and π···π interactions (magenta dashed lines).

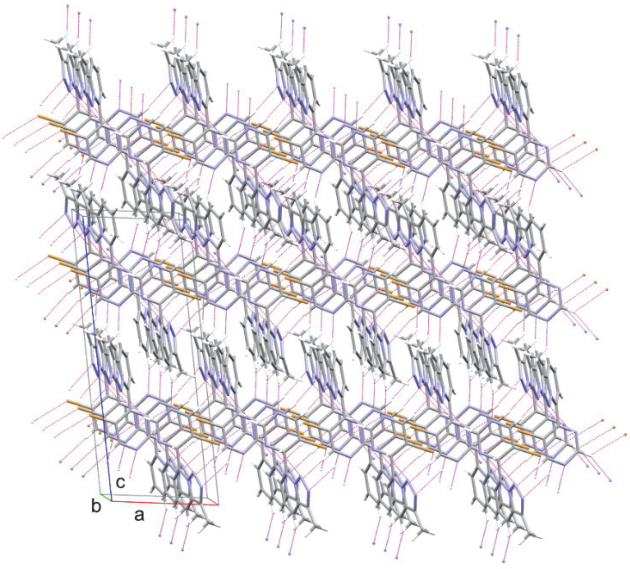


Figure S3. View of the 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-a]pyridine 3D framework. C-H···X (X = Br, N) contacts (magenta dashed lines) are depicted.

3. Fluorescence and UV-Vis study

UV/Vis and Fluorescence titration of 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine with Zn(II) and Cu(II) lead to the conclusion that the corresponding M_2L_2 complexes cannot be detected by these techniques (NMR also afforded negative results). Not significant variations of the absorption spectra were recorded when copper or zinc (divalent salts) was added. However, in fluorescence, small quenching was observed and the corresponding Stern Volmer constants were calculated (for a 1 to 1 stoichiometry) being: 213 M^{-1} for Zn(II) and 177 M^{-1} for Cu(II). The lack of a complete quenching of the fluorescence with Cu(II) clearly indicates that these complex have relatively small constants.

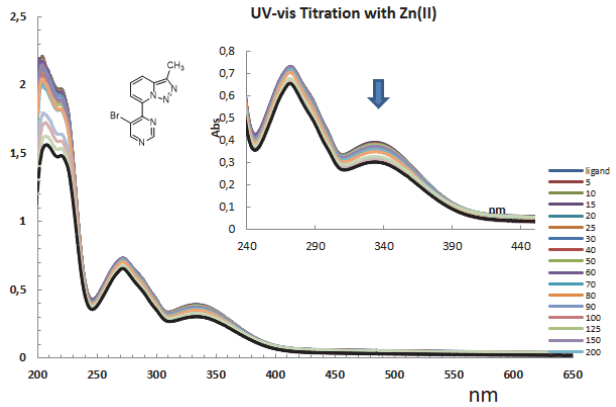


Figure S4. UV-vis titration of 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-a]pyridine with Zn(II).

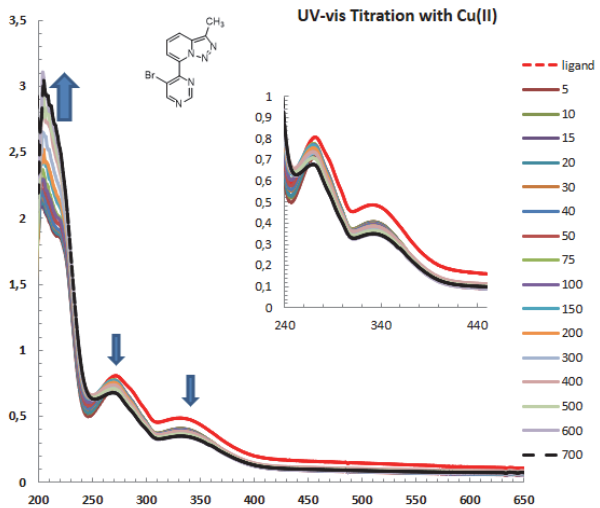


Figure S5. UV-vis titration of 7-(5-bromopyrimidin-4-yl)-3-methyl-[1,2,3]triazolo[1,5-a]pyridine with Cu(II).

4. NCI plots and AIM intermolecular parameters for $[(ZnCl_2)_2(\mu\text{-bptpy})_2]$ (2)

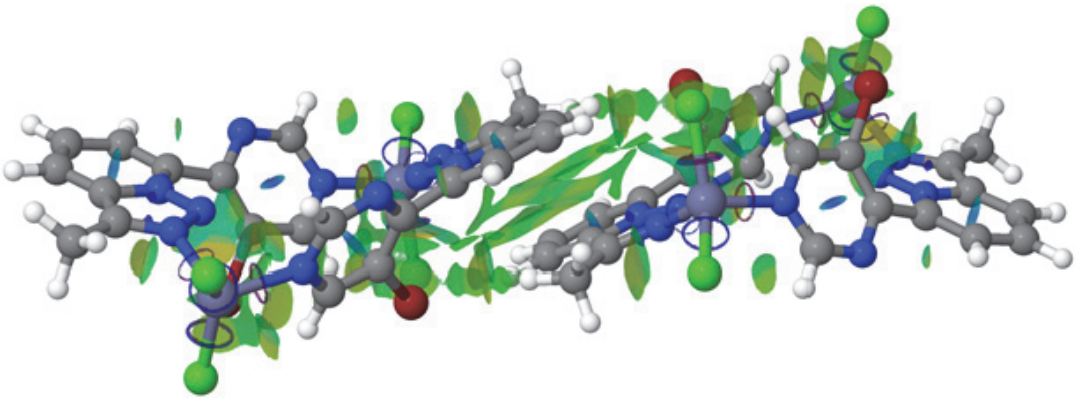


Figure S6. NCI plot of the $[(ZnCl_2)_2(\mu\text{-bptpy})_2]_2$ dimer. Gradient isosurface value shown: 0.5 au. The surfaces are coloured on a blue-green-red scale according to values of sign(λ^2)ρ, ranging from +0.03 to -0.03 au.

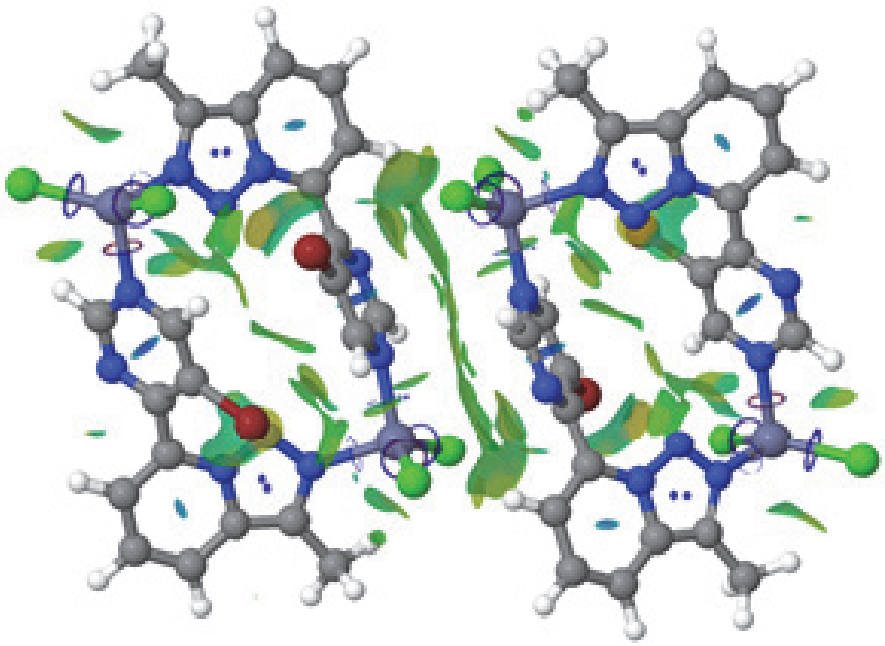


Figure S7. NCI plot for the second $[(ZnCl_2)_2(\mu\text{-bptpy})_2]_2$ dimer considered. Gradient isosurface value shown: 0.5 au. The surfaces are coloured on a blue-green-red scale according to values of sign(λ^2)ρ, ranging from +0.03 to -0.03 au.

Table S2. Electron density properties (au) of the intermolecular BCPs shown in Fig. 7.

Atoms	Dist (Å)	Rho	Lap	G	V	H
H38-Cl88	2.847	0.0080	0.0288	0.0056	-0.0039	0.0016
Cl32-H94	2.847	0.0080	0.0288	0.0056	-0.0039	0.0016
C93-C35	3.312	0.0061	0.0184	0.0037	-0.0028	0.0009
C91-C37	3.312	0.0061	0.0184	0.0037	-0.0028	0.0009
Br86-H38	3.226	0.0035	0.0112	0.0021	-0.0014	0.0007
Br86-H55	2.903	0.0080	0.0240	0.0048	-0.0036	0.0012
Cl88-H40	2.713	0.0100	0.0364	0.0073	-0.0054	0.0018
H96-Cl32	2.713	0.0100	0.0364	0.0073	-0.0054	0.0018
C95-H56	2.835	0.0062	0.0207	0.0040	-0.0028	0.0012
H94-Br30	3.226	0.0035	0.0112	0.0021	-0.0014	0.0007
H111-Br30	2.903	0.0080	0.0240	0.0048	-0.0036	0.0012
H112-C39	2.835	0.0062	0.0207	0.0040	-0.0028	0.0012
max	3.312	0.0100	0.0364	0.0073	-0.0014	0.0018
min	2.713	0.0035	0.0112	0.0021	-0.0054	0.0007

Table S3. Electron density properties (au) of the intermolecular BCPs shown in Fig. 9.

Atoms	Dist	Rho	Lap	G	V	H
C74-N17	3.512	0.0037	0.0123	0.0025	-0.0019	0.0006
C78-Cl31	3.376	0.0077	0.0255	0.0050	-0.0037	0.0013
C69-Cl31	3.608	0.0052	0.0160	0.0032	-0.0023	0.0008
H70-Cl32	2.654	0.0105	0.0356	0.0074	-0.0059	0.0015
N73-C18	3.512	0.0037	0.0123	0.0025	-0.0019	0.0006
N76-Cl32	3.890	0.0031	0.0096	0.0019	-0.0014	0.0005
Cl87-C22	3.376	0.0077	0.0255	0.0050	-0.0037	0.0013
Cl87-C13	3.608	0.0052	0.0160	0.0032	-0.0023	0.0008
Cl88-H14	2.654	0.0105	0.0356	0.0074	-0.0059	0.0015
Cl88-N20	3.890	0.0031	0.0096	0.0019	-0.0014	0.0005
max	3.890	0.0105	0.0356	0.0074	-0.0014	0.0015
min	2.654	0.0031	0.0096	0.0019	-0.0059	0.0005

[1]J. D. Bower and G. R. Ramage , *J. Chem. Soc.*, 1957, 4506.

[2] Bondi A. *J. Phys. Chem.*1964, **68**, 441; D. A. Safinn, M. G. Babashkina, K. Robeyns and Y. Garcia, *RSC Adv.*,2016, **6**, 53669.