Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Deep-Blue Fluorophores with Imidazoacridine Acceptors: Enhancing Photostablility and Two-Photon Fluorescence using Structural Constraint

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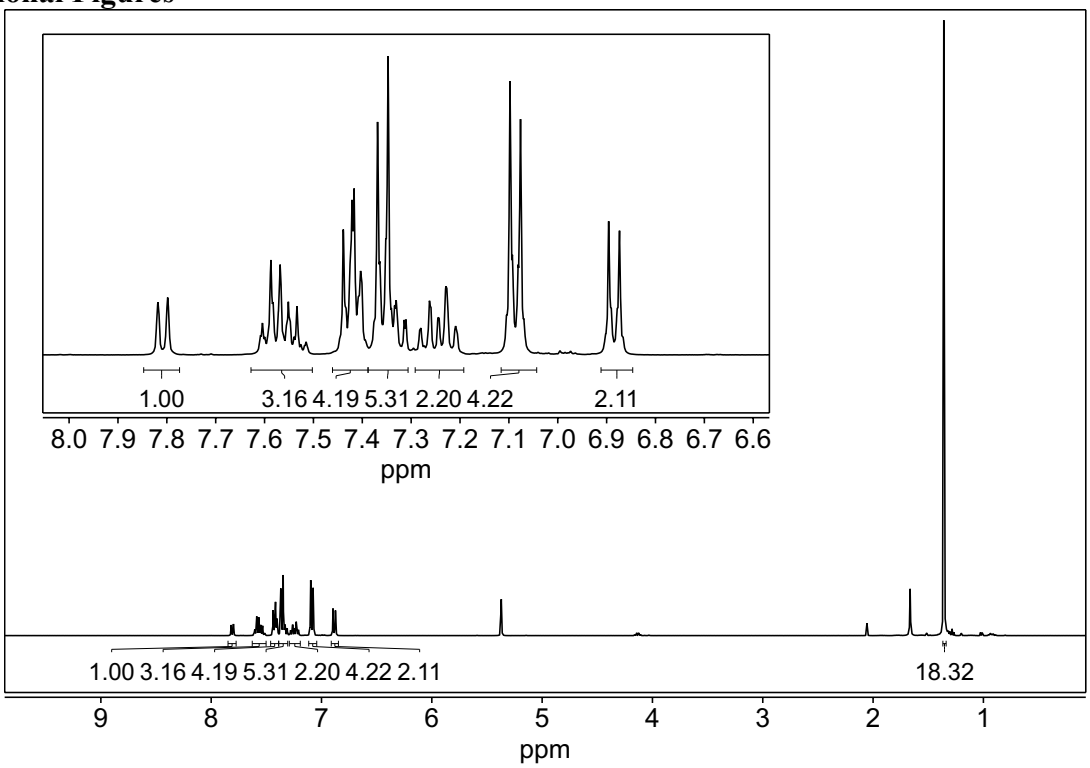


Figure S1 ^{1}H NMR spectrum of **tBuTPA-PBI** in **methylene chloride-*d*$_2$**.

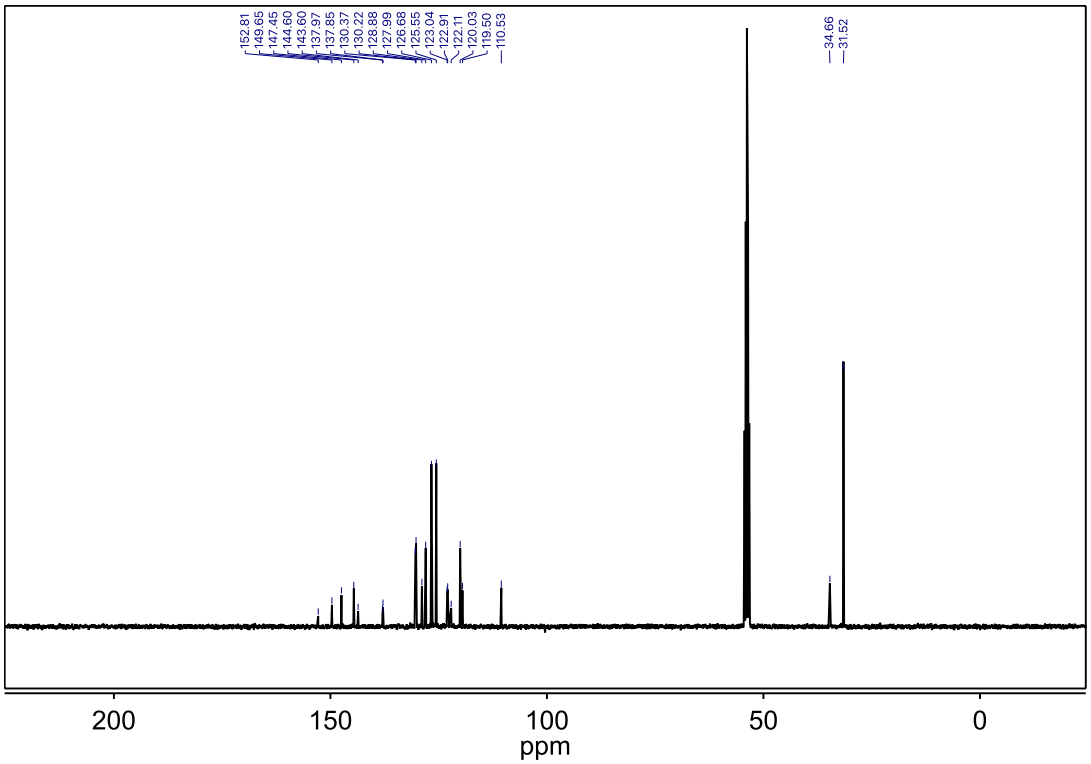


Figure S2 ^{13}C{^{1}H} NMR spectrum of **tBuTPA-PBI** in **methylene chloride-*d*$_2$**.

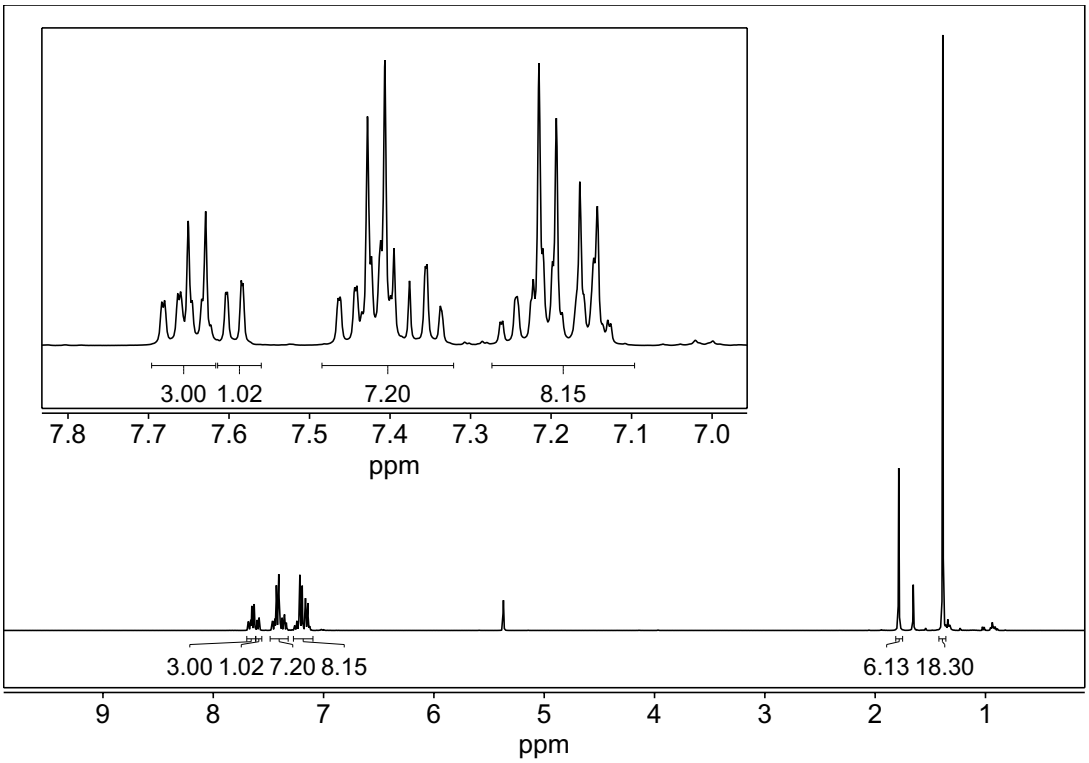


Figure S3 ^{1}H NMR spectrum of **tBuTPA-IMAC** in **methylene chloride-*d*$_2$**.

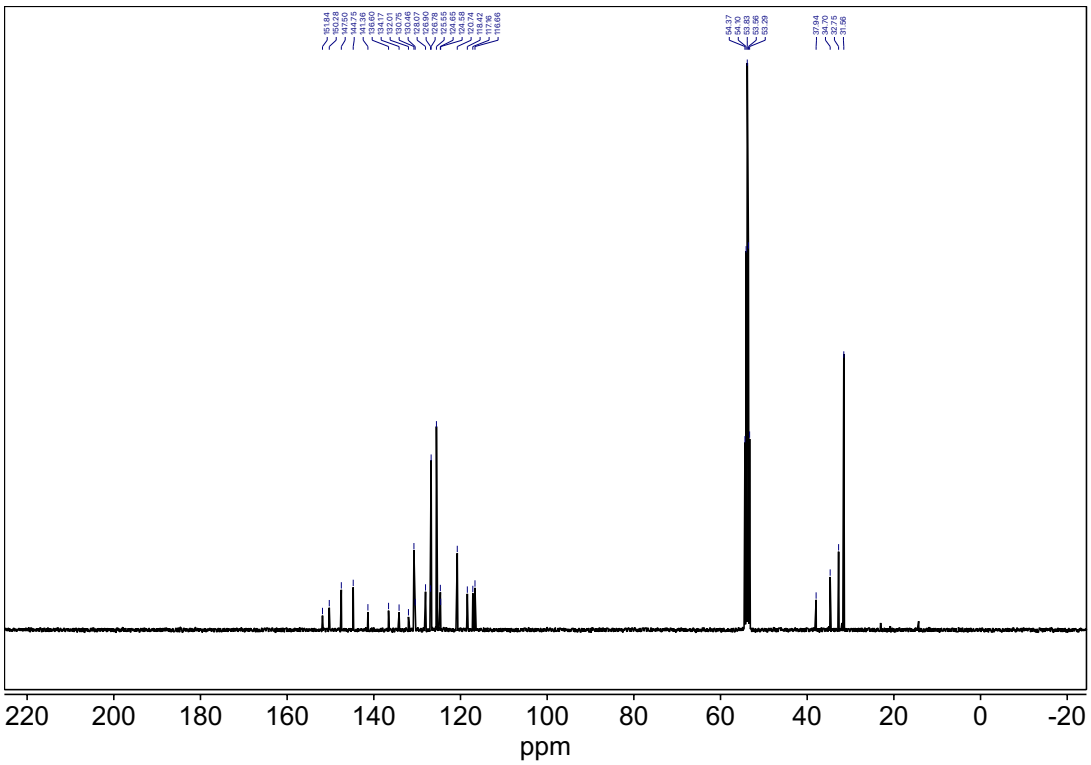
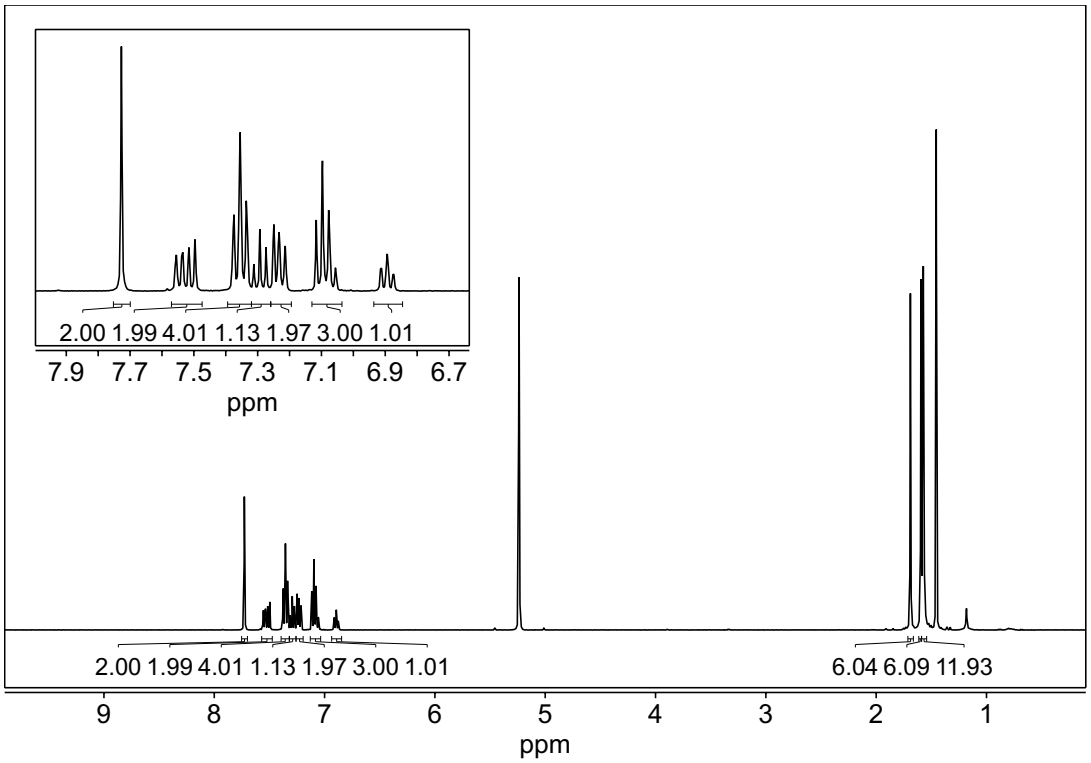


Figure S4 ^{13}C{^{1}H} NMR spectrum of **tBuTPA-IMAC** in **methylene chloride-*d*$_2$**.



$^{13}C\{^{1}H\}$ NMR spectrum of **HMAT-IMAC** in **methylene chloride-d_2**.

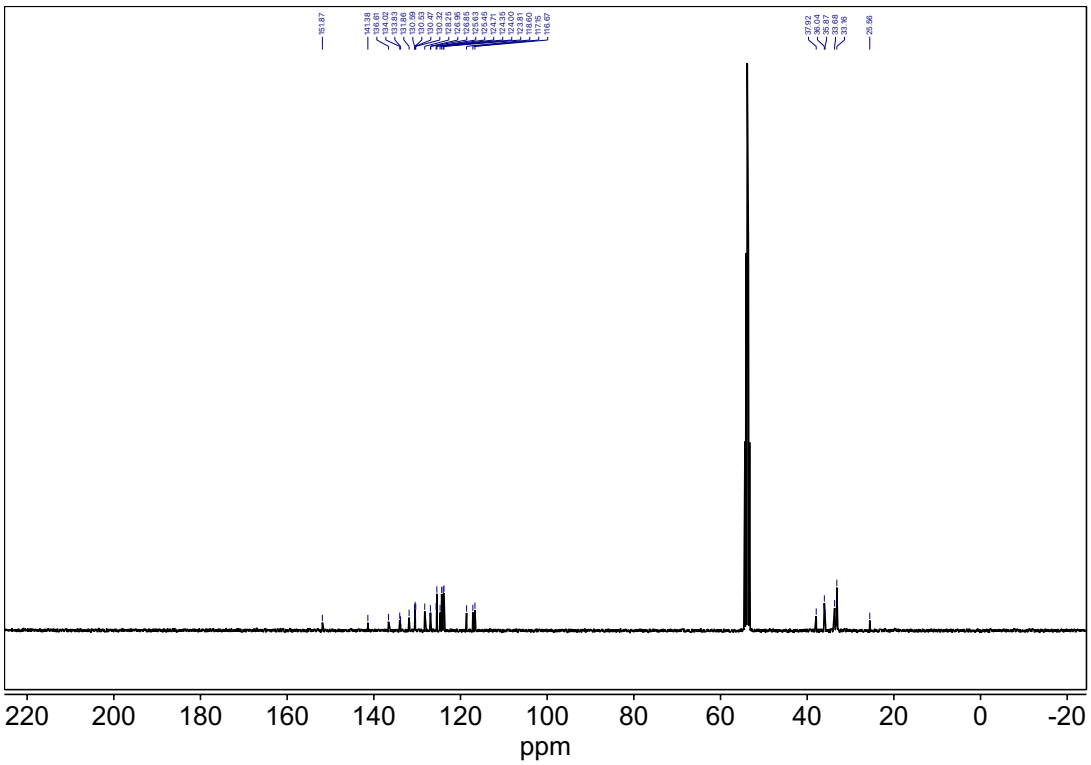


Figure S5 $^{13}C\{^{1}H\}$ NMR spectrum of **HMAT-IMAC** in **methylene chloride-d_2**.

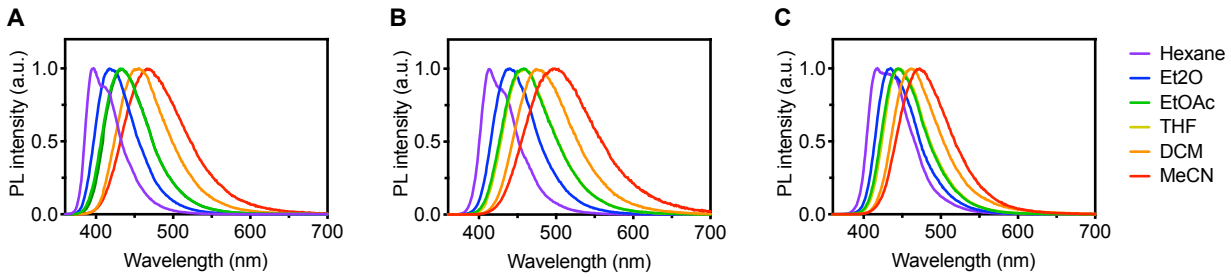


Figure S6 Emission spectra showing solvatochromic shifts in various solvents, where (A) is **tBuTPA-PBI**, (B) is **tBuTPA-IMAC**, (C) is **HMAT-IMAC**.

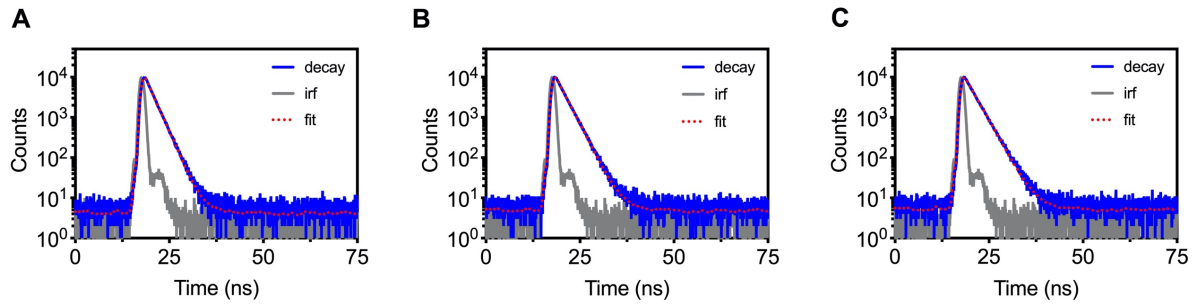


Figure S7: PL decay curves of (A) **tBuTPA-PBI**, (B) **tBuTPA-IMAC**, and (C) **HMAT-IMAC** measured as a solution in toluene at 300 K.

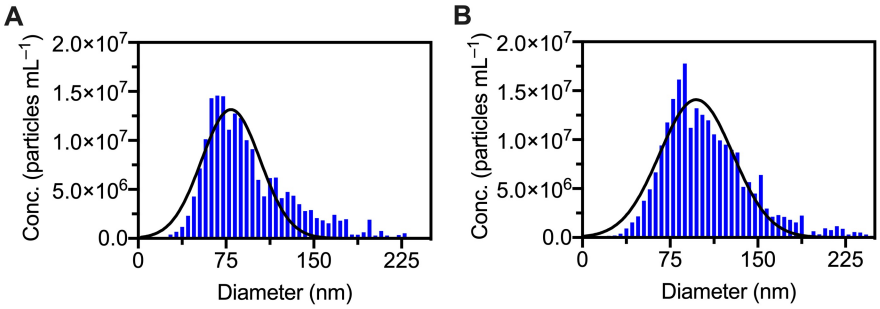


Figure S8: Size distribution of polymer dots of (A) **tBuTPA-PBI** and (B) **tBuTPA-IMAC** in aqueous solution (blue) with curve fit (solid black line) at 0.25 μg mL^{-1}.

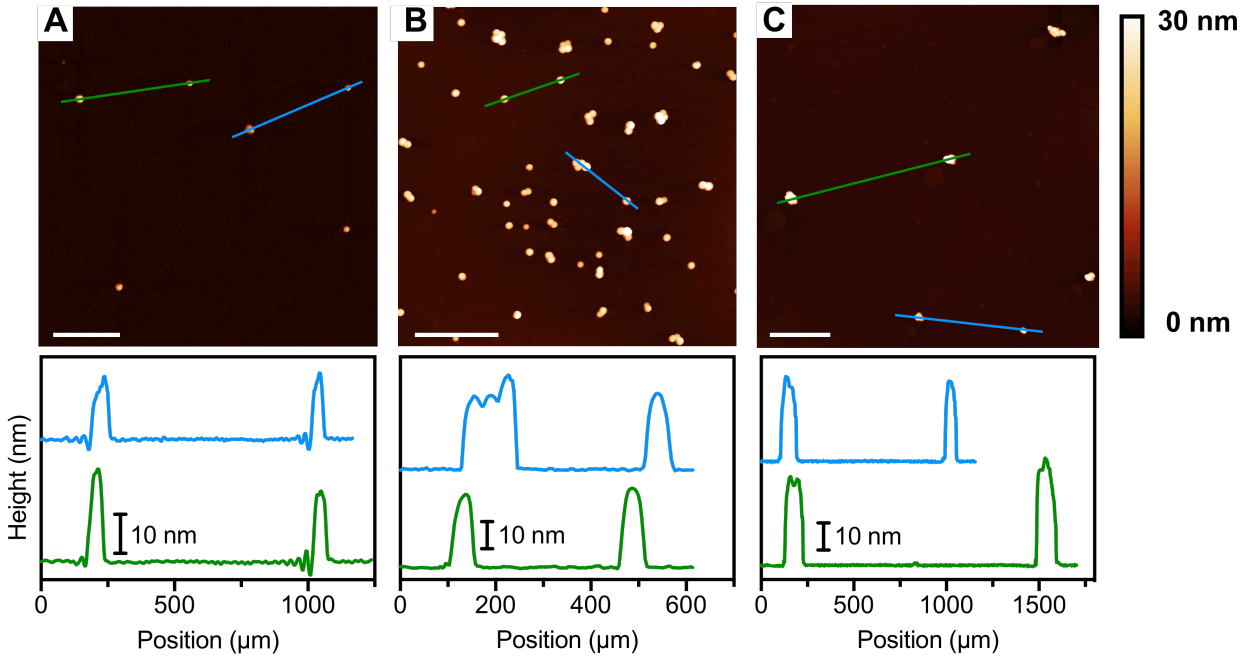


Figure S9: AFM height images of polymer dots of (A) **tBuTPA-PBI**, (B) **tBuTPA-IMAC**, and (C) **HMAT-IMAC** in aqueous solution cast on mica (scale bar = 0.5 µm). Selected height profiles for the lines indicated in the image are shown below.

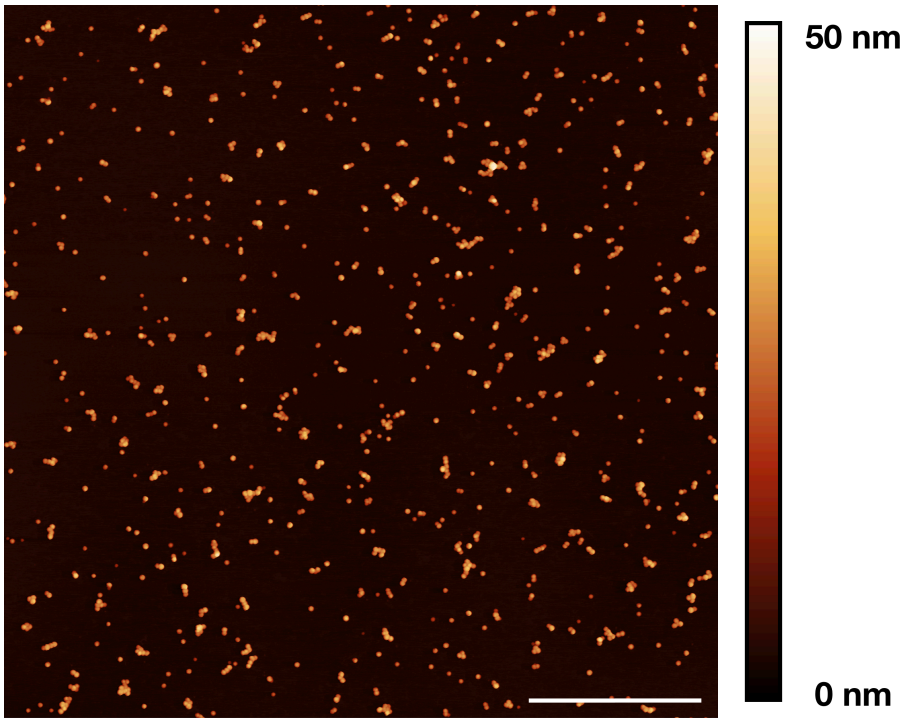
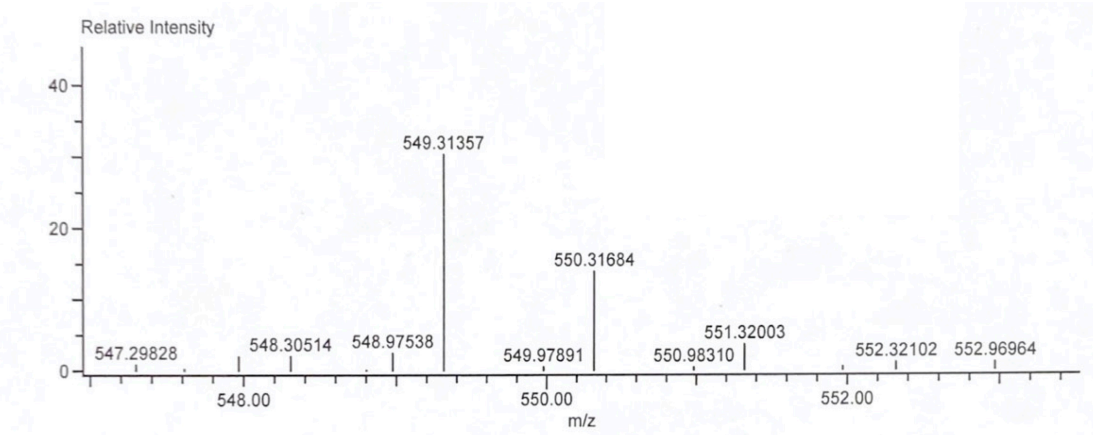
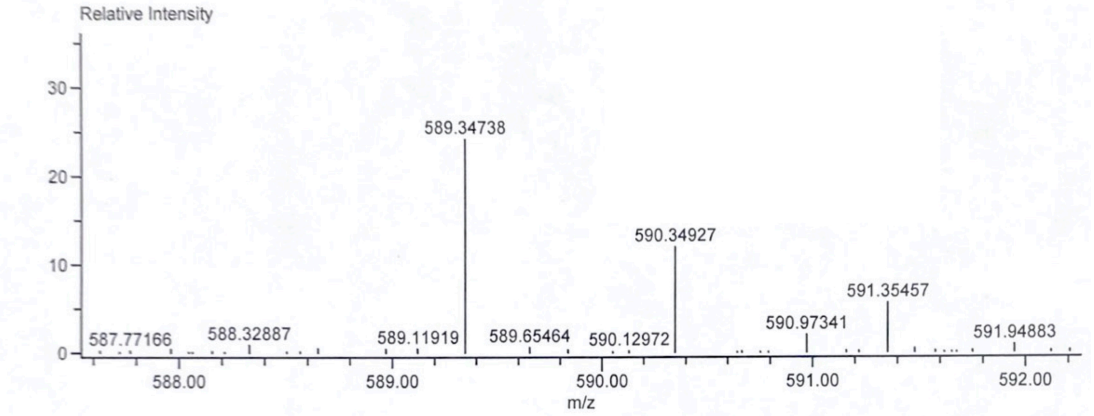


Figure S10: Large area AFM height image of polymer dots of **tBuTPA-IMAC** in aqueous solution cast on mica (scale bar = 1.5 µm). Many small sphere-shaped objects can be observed (average diameter = 53 nm, standard deviation = 22 nm).



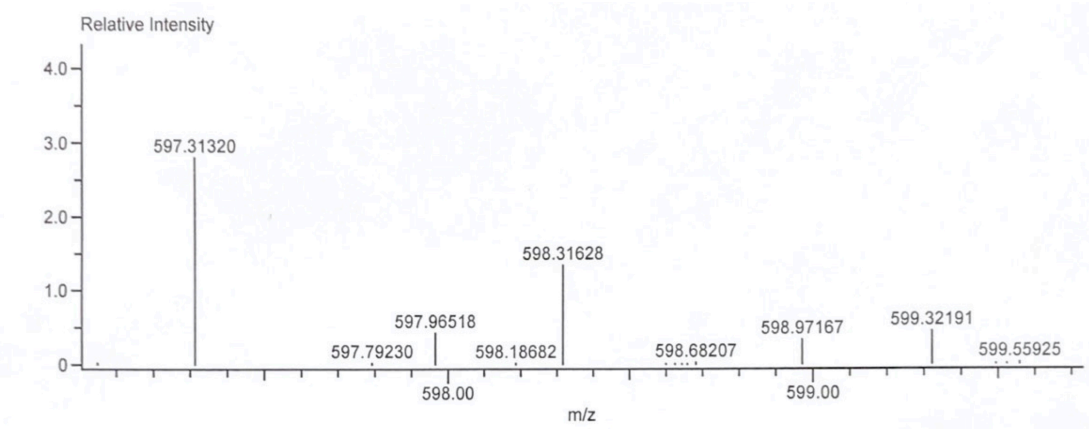
Mass	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
549.31357	549.31440	-0.82	-1.50	$^{12}C_{39}{}^{1}H_{39}{}^{14}N_3$	22.0

Figure S11: Mass spectrum of **tBuTPA-PBI**.



Mass	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
589.34738	589.34570	1.68	2.86	$^{12}C_{42}{}^{1}H_{43}{}^{14}N_3$	23.0

Figure S12: Mass spectrum of **tBuTPA-IMAC**.



Mass	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
597.31320	597.31440	-1.20	-2.01	$^{12}C_{43}{}^{1}H_{39}{}^{14}N_3$	26.0

Figure S13: Mass spectrum of **HMAT-IMAC**.

Table S1 Calculated and experimental electronic properties of the series of IMAC compounds.

Entry	$E_{1/2}^{ox}$[a]	$E_{1/2}^{red}$[a]	HOMO (eV)		LUMO (eV)		E_g (eV)	
			Calc.	Exp.[b]	Calc.	Exp.[b]	Calc.	Exp.[c]
tBuTPA-PBI	0.49	–	–5.04	–5.29	–0.88	–	3.58	3.16
tBuTPA-IMAC	0.49	–2.66	–5.11	–5.29	–1.03	–2.14	3.50	3.08
HMAT-IMAC	0.44	–2.60	–5.03	–5.24	–1.05	–2.20	3.39	3.05

[a]In DMF relative to $FeCp^{0/+}$.
[b]Calculated from $E_{1/2}^{ox}$ relative to the $FeCp^{0/+}$ HOMO level (–4.80 eV).
[c]Calculated from the LUMO level and the optical energy gap, E_g. E_g was determined from the intersection point of the normalized emission and absorption spectra.

Table S2 TD-DFT results for the HOMO to LUMO transition in IMAC compounds.

Entry	Total Energy (Hartree)[a]	λ (nm)[b]	ΔE (eV)[b]	f[b]
tBuTPA-PBI	–1671.97	346	3.58	0.9645
tBuTPA-IMAC	–1788.55	354	3.50	0.8898
HMAT-IMAC	–1824.28	349	3.39	0.5653

[a]Calculated total energy of the optimized structures in S_0. [b]Calculated with TDA-DFT on neutral condition optimized structures in S_1.

Table S3 Cartesian Coordinates [Å] of the Optimized Structures for **tBuTPA-PBI** in S_0.

Atom	X	Y	Z	Atom	X	Y	Z
C	2.64565	3.38667	-1.33001	H	-9.38639	-0.60266	-0.72632
C	3.68055	3.73792	-0.45917	N	-4.33144	-1.29336	-1.82208
C	4.06779	2.77405	0.4824	H	-5.54866	3.47946	2.79926
C	3.45392	1.53298	0.56072	H	-4.40426	2.34138	4.68662

C	2.03217	2.13875	-1.2765	H	-3.45277	0.07087	4.36438
C	2.42396	1.19563	-0.32477	H	-3.65685	-1.06119	2.16185
C	3.81682	-1.36201	-0.77713	H	4.86411	2.99809	1.18811
N	1.80531	-0.07529	-0.25793	C	4.38247	5.09621	-0.49946
C	2.61106	-1.22537	-0.08729	H	3.77115	0.81252	1.30906
C	4.61531	-2.4864	-0.59132	H	4.1312	-0.58003	-1.46218
C	4.2419	-3.52264	0.26838	H	1.29631	-2.15724	1.34055
C	3.02486	-3.37113	0.94781	H	0.48129	-2.07339	-1.43599
C	2.22685	-2.24836	0.78778	H	-0.01843	1.66501	0.61944
H	2.30745	4.08792	-2.08606	H	1.24023	1.893	-1.97814
H	5.54418	-2.54886	-1.14903	H	-5.7131	2.35351	0.58756
C	5.09091	-4.77605	0.48588	H	-7.60158	0.37175	0.70467
H	2.69097	-4.14382	1.63614	C	4.20381	5.80491	0.85312
H	-1.97499	-2.27204	-1.64296	H	3.14289	5.97338	1.06915
C	-1.53693	-1.42183	-1.12971	H	4.70929	6.77832	0.84299
C	-0.16252	-1.30475	-1.02006	H	4.62428	5.21969	1.67778
C	0.41103	-0.19502	-0.37972	C	5.88159	4.88962	-0.77051
C	-0.44233	0.79419	0.12955	H	6.35414	4.27648	0.00414
C	-1.81844	0.67593	0.00773	H	6.40121	5.85531	-0.79522
H	-2.44485	1.47107	0.39837	H	6.03977	4.39207	-1.73384
C	-2.39462	-0.44043	-0.6124	C	3.82	6.00681	-1.59401
C	-3.83467	-0.61262	-0.81517	H	2.75526	6.21725	-1.44142
C	-6.70741	-1.75004	-2.49318	H	3.94516	5.57004	-2.5914
C	-8.02455	-1.51606	-2.12703	H	4.35096	6.9653	-1.58423
C	-8.34308	-0.75905	-0.9863	C	6.3775	-4.7552	-0.34344
C	-7.35498	-0.20627	-0.18094	H	6.16825	-4.71156	-1.41839
C	-5.69697	-1.20557	-1.69502	H	6.95136	-5.66957	-0.15553
C	-6.0364	-0.43601	-0.56449	H	7.01687	-3.9042	-0.08208
C	-5.23018	1.85964	1.42589	C	5.47821	-4.88085	1.97
N	-4.82357	-0.06154	-0.00613	H	6.06556	-4.0105	2.28328
C	-4.69363	0.58373	1.25055	H	6.08107	-5.78054	2.14398
C	-5.12989	2.48604	2.6648	H	4.59683	-4.94027	2.61728
C	-4.48691	1.84815	3.72227	C	4.28061	-6.01897	0.08326
C	-3.95118	0.57483	3.54108	H	3.99634	-5.97495	-0.974
C	-4.06074	-0.0647	2.31141	H	3.36248	-6.11438	0.67252
H	-6.45233	-2.3404	-3.36797	H	4.87395	-6.9281	0.24006
H	-8.82956	-1.92764	-2.72964				

Table S4 Cartesian Coordinates [Å] of the Optimized Structures for **tBuTPA-IMAC** in S_0.

Atom	X	Y	Z	Atom	X	Y	Z
C	3.16276	3.53008	-1.13727	H	-4.90792	0.27949	4.95886
C	4.14335	3.88391	-0.20671	H	-2.70044	-0.49518	4.08282
C	4.53335	2.8946	0.70697	H	-2.38287	-0.7809	1.66043
C	3.97229	1.62636	0.70289	C	-6.82521	0.55838	0.68288
C	2.60354	2.25609	-1.1665	C	-6.80408	2.06858	0.35854
C	2.99616	1.28782	-0.24093	H	-5.86614	2.35238	-0.12943

C	4.51265	-1.18459	-0.76897	H	-6.90546	2.65832	1.27709
N	2.43164	-0.01023	-0.25754	H	-7.62936	2.32314	-0.31623
C	3.28224	-1.13176	-0.11232	C	-8.16936	0.20746	1.32988
C	5.3545	-2.28082	-0.60746	H	-8.19938	-0.83963	1.64707
C	5.00207	-3.36979	0.19393	H	-8.98276	0.37383	0.61727
C	3.76013	-3.30166	0.84104	H	-8.38236	0.84191	2.19544
C	2.91811	-2.20825	0.70505	H	5.28866	3.11923	1.45618
H	2.82596	4.25081	-1.87535	C	4.78436	5.27159	-0.15454
H	6.30139	-2.27813	-1.13763	H	4.28941	0.88579	1.43142
C	5.89915	-4.59401	0.38306	H	4.81195	-0.35944	-1.40866
H	3.44101	-4.11812	1.48433	H	1.96868	-2.18225	1.23205
H	-1.19211	-2.304	-1.88094	H	1.24248	-2.01238	-1.56306
C	-0.81331	-1.45909	-1.31438	H	0.5043	1.61802	0.61335
C	0.55027	-1.28914	-1.14373	H	1.8538	2.00977	-1.91294
C	1.05056	-0.18288	-0.43912	C	4.22885	6.20724	-1.23135
C	0.13677	0.75019	0.07513	H	4.41648	5.82356	-2.24072
C	-1.22603	0.57801	-0.10753	H	4.71502	7.18622	-1.15457
H	-1.91087	1.32236	0.28932	H	3.15014	6.36428	-1.11757
C	-1.72828	-0.53757	-0.79005	C	4.5155	5.90743	1.21916
C	-3.1534	-0.71183	-1.07684	H	3.43971	6.01943	1.39443
C	-5.93503	-1.3944	-3.14437	H	4.97613	6.90127	1.27579
C	-7.2541	-1.12713	-2.79554	H	4.92617	5.30291	2.0348
C	-7.60988	-0.54057	-1.56556	C	6.30156	5.14275	-0.36669
C	-6.64311	-0.20375	-0.62026	H	6.52356	4.6982	-1.34326
C	-4.94883	-1.07069	-2.20818	H	6.76768	4.51517	0.40024
C	-5.34697	-0.50315	-0.99581	H	6.77743	6.13011	-0.32464
C	-5.64066	0.25533	1.61925	C	6.24938	-4.74642	1.87226
N	-4.20517	-0.30027	-0.2514	H	6.78888	-3.86614	2.23927
C	-4.36438	-0.12802	1.1444	H	6.8863	-5.62611	2.02581
C	-5.78739	0.39572	3.00093	H	5.35388	-4.87172	2.49011
C	-4.74802	0.15342	3.89193	C	7.20593	-4.48197	-0.40638
C	-3.5182	-0.26876	3.4045	H	7.80037	-3.61727	-0.08977
C	-3.33151	-0.42008	2.03738	H	7.02475	-4.39951	-1.48416
H	-5.6767	-1.834	-4.10263	H	7.81355	-5.37874	-0.24129
H	-8.04563	-1.36717	-3.5004	C	5.15565	-5.8517	-0.09543
H	-8.65989	-0.33937	-1.37351	H	4.22683	-6.01201	0.46212
N	-3.57426	-1.17561	-2.2329	H	5.7839	-6.74053	0.04016
H	-6.74907	0.70157	3.39941	H	4.89896	-5.77394	-1.15778

Table S5 Cartesian Coordinates [Å] of the Optimized Structures for **HMAT-IMAC** in S_0.

Atom	X	Y	Z	Atom	X	Y	Z
C	-3.13578	-3.60011	-0.99351	H	4.93878	4.20903	-1.63876
C	-4.48544	-3.89656	-0.96083	H	7.32468	3.50325	-1.60789
C	-5.36149	-2.87798	-0.63648	H	8.00387	1.27476	-0.88039
C	-4.92538	-1.58487	-0.35041	N	2.89497	2.363	-0.76344
C	-2.64818	-2.32456	-0.71295	H	6.23943	-2.92491	1.72539

C	-3.5472	-1.28787	-0.38623	H	4.44861	-3.79242	3.15358
C	-5.99398	-0.56704	-0.01082	H	2.2189	-2.66451	3.16078
C	-5.38406	0.79154	0.26384	H	1.82902	-0.72696	1.69664
N	-3.07743	0.01904	-0.10187	C	6.23429	-0.86562	-0.05299
C	-3.99882	1.05024	0.214	C	6.20622	-1.68312	-1.36333
C	-6.26866	1.82215	0.57969	H	5.25462	-1.55137	-1.88821
C	-5.83724	3.10791	0.84557	H	6.33653	-2.75069	-1.15089
C	-4.47853	3.3563	0.79229	H	7.01125	-1.3564	-2.03139
C	-3.55258	2.36032	0.48588	C	7.59681	-1.05525	0.62266
H	-2.42888	-4.38491	-1.24468	H	7.63422	-0.55417	1.59499
H	-4.84542	-4.89684	-1.18193	H	8.38862	-0.64028	-0.00814
C	-1.1458	-2.14303	-0.77615	H	7.83726	-2.11315	0.76436
H	-7.3316	1.60409	0.616	H	-6.42603	-3.08839	-0.60252
H	-6.5425	3.89732	1.08743	C	-6.75721	-1.03957	1.24537
H	-4.11655	4.35967	0.99424	H	-6.07609	-1.12813	2.09768
C	-2.09542	2.77177	0.46219	H	-7.22452	-2.01564	1.08091
H	0.5341	2.8376	0.29086	H	-7.54964	-0.33452	1.5156
C	0.16169	1.83664	0.10235	C	-6.97118	-0.4478	-1.20048
C	-1.20491	1.59126	0.13558	H	-7.44482	-1.40907	-1.42279
C	-1.69539	0.29423	-0.13439	H	-6.4428	-0.11335	-2.09884
C	-0.75886	-0.71679	-0.44313	H	-7.76846	0.2711	-0.98787
C	0.59998	-0.42195	-0.46258	C	-1.70457	3.32849	1.84807
H	1.29911	-1.20993	-0.72342	C	-1.89555	3.86155	-0.6129
C	1.09438	0.84588	-0.17904	C	-0.6554	-2.47922	-2.20078
C	2.51003	1.20138	-0.28226	C	-0.48287	-3.09464	0.24334
C	5.22635	3.22117	-1.29284	H	-0.8511	4.18539	-0.65835
C	6.55532	2.81334	-1.2717	H	-2.50915	4.74273	-0.39985
C	6.94868	1.53004	-0.84522	H	-2.17626	3.48258	-1.60068
C	6.01169	0.59631	-0.40723	H	-1.11445	-1.80801	-2.93343
C	4.26962	2.30265	-0.85146	H	-0.91129	-3.50753	-2.47447
C	4.70487	1.04645	-0.4237	H	0.4315	-2.37757	-2.28079
C	5.07869	-1.35483	0.83977	H	0.60714	-2.99293	0.23631
N	3.58657	0.34624	-0.02556	H	-0.71875	-4.13994	0.02045
C	3.78955	-0.77296	0.81657	H	-0.838	-2.87678	1.25603
C	5.26703	-2.4448	1.69255	H	-0.65836	3.64875	1.86449
C	4.25649	-2.93941	2.50921	H	-1.84021	2.56557	2.62139
C	3.01417	-2.31872	2.50648	H	-2.31822	4.19451	2.11455
C	2.78642	-1.23223	1.6726				

X-ray Crystallography Methods

(tBuTPA-PBI)$_2$CuBr$_2$. $CuBr_2$ (2.0 mg, 0.0091 mmol) and **tBuTPA-PBI** (10.0 mg, 0.0182 mmol) were dissolved in 0.2 mL of NMP and stirred for 30 mins. The solution was then heated to 70 °C and placed under vacuum (pressure reduced to 25 torr) for 1 h to concentrate the NMP. Benzene

was added (0.5 mL) followed by hexanes (1.0 mL) and the solution was left to slowly evaporate, giving crystals suitable for X-ray diffraction analysis.

A brown tablet-shaped crystal with dimensions 0.18 × 0.15 × 0.06 mm^3 was mounted on a mylar loop in oil. Data were collected using a Bruker APEX II area detector diffractometer equipped with a Kryoflex low-temperature device operating at T = 120(2) K. Data were measured using φ and ω scans of 0.5 ° per frame for 30 s using MoK_α radiation (microfocus sealed X-ray tube, 50 kV, 0.99 mA). The total number of runs and images was based on the strategy calculation from the program APEX3. The maximum resolution that was achieved was Θ = 29.784° (0.72 Å). The unit cell was refined using SAINT[1] on 9966 reflections, 19% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT.[1] The final completeness is 100.00 % out to 29.784° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2[2] was used for absorption correction. wR_2(int) was 0.0816 before and 0.0445 after correction. The ratio of minimum to maximum transmission is 0.9092. The λ /2 correction factor is not present. The absorption coefficient μ of this material is 1.119 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.855 and 0.940.

The structure was solved and the space group P-1 (# 2) determined by the **XT**[3] structure solution program using Intrinsic Phasing methods and by using **Olex2**[5] as the graphical interface. The model was refined by full matrix least squares minimisation on F^2 using version 2018/3 of **XL**.[4] The material crystallizes with three molecules of benzene in the asymmetric unit, or six in the unit cell. Additionally, there appears to be a site that is partially occupied by water, with an occupancy of ~0.18. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

(tBuTPA-IMAC)$_2$CuBr$_2$. $CuBr_2$ (1.9 mg, 0.0085 mmol) and **tBuTPA-IMAC** (10.0 mg, 0.0170 mmol) were dissolved in 0.2 mL of NMP and stirred for 30 mins. The solution was then heated to 70 °C and placed under vacuum (pressure reduced to 25 torr) for 1 h to concentrate the NMP. Benzene was added (0.5 mL) followed by hexanes (1.0 mL) and the solution was left to slowly evaporate, giving crystals suitable for X-ray diffraction analysis.

Single brown prism crystals of **tBuTPA-IMAC** were recrystallised from a mixture of

benzene and hexane by slow evaporation. A suitable crystal with dimensions 0.28 × 0.09 × 0.05 mm^3 was mounted on a mylar loop in oil. Data were collected using a Bruker APEX II area detector diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110(2) K. Data were measured using φ and ω scans of 0.5 ° per frame for 30 s using MoK$_\alpha$ radiation (TRIUMPH monochromator, sealed X-ray tube, 45kV, 30mA). The total number of runs and images was based on the strategy calculation from the program APEX3. The maximum resolution that was achieved was Θ = 26.464° (0.80 Å). The unit cell was refined using SAINT[1] on 9980 reflections, 22% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT.[1] The final completeness is 100.00 % out to 26.464° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2[2] was used for absorption correction. wR_2(int) was 0.0412 before and 0.0341 after correction. The ratio of minimum to maximum transmission is 0.9184. The λ/2 correction factor is not present. The absorption coefficient μ of this material is 1.216 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.864 and 0.941.

The structure was solved and the space group *P*-1 (# 2) determined by the **XT**[3] structure solution program using Intrinsic Phasing methods and by using **Olex2**[5] as the graphical interface. The model was refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of **XL**.[4] The material crystallizes with one half-molecule in the asymmetric unit, with the Cu atom residing on an inversion center. The material also crystallizes with one molecule of benzene in the asymmetric unit, in addition to what appears to be a partially occupied site with solvent NMP. Unfortunately, the disorder in the NMP site appears to be either disordered or partially occupied by some other solvent molecule, presumably hexane. A stable model that accounted for both the NMP molecule and whatever else resides at that site could not be achieved, and thus the PLATON/SQUEEZE[6] program was used to generate a data set free from solvent at that site. Finally, one t-butyl fragment was also disordered by rotation about the C36—C39 bond. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

(HMAT-IMAC)$_2$CuBr$_2$. $CuBr_2$ (1.2 mg, 0.0054 mmol) and **HMAT-IMAC** (6.4 mg, 0.0107

mmol) were dissolved in 0.2 mL of NMP and stirred for 30 mins. The solution was then heated to 70 °C and placed under vacuum (pressure reduced to 25 torr) for 1 h to concentrate the NMP. Benzene was added (0.4 mL) followed by layering with heptanes (1.0 mL) and the solution was left to slowly evaporate, giving crystals suitable for X-ray diffraction analysis.

A brown tablet-shaped crystal with dimensions 0.17 × 0.16 × 0.06 mm^3 was mounted on a mylar loop in oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110(2) K. Data were measured using φ and ω scans of 1.0 ° per frame for between 5 and 20 s using CuK_α radiation (microfocus sealed X-ray tube, 45 kV, 0.60 mA). The total number of runs and images was based on the strategy calculation from the program APEX3. The maximum resolution that was achieved was Θ = 68.442° (0.83 Å). The unit cell was refined using SAINT[1] on 9682 reflections, 69% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT.[1] The final completeness is 99.50 % out to 68.442° in Θ. The material crystallizes as a two-component split-crystal, with an approximate ratio of 80:20 between the major and minor domains, A multi-scan absorption correction was performed using TWINABS-2012/1 (Bruker, 2012) was used for absorption correction. Final HKLF 4 output contains 117330 reflections, R_{int} = 0.0714 (59258 with I > 3sig(I), R_{int} = 0.0621). The absorption coefficient μ of this material is 2.025 mm^{-1} at this wavelength (λ = 1.54178Å) and the minimum and maximum transmissions are 0.690 and 0.886.

The structure was solved and the space group P-1 (# 2) determined by the **XT**[3] structure solution program using Intrinsic Phasing methods and by using **Olex2**[5] as the graphical interface. The model was refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of **XL**,[4] using an HKLF4 format data set containing reflections from the major twin domain only. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There are two crystallographically independent half-molecules in the asymmetric unit. Each resides on a separate inversion center, generating the other half of the molecule. Additionally, there are two molecules of benzene in the asymmetric unit, or four molecules in the unit cell.

All graphic plots were produced using Mercury version 3.9. See Table S6. In addition, CCDC 2063778-2063780 contain the supplementary crystallographic data for this paper. These data are

provided free of charge by The Cambridge Crystallographic Data Centre.

Table S6 X-ray diffraction collection data and refinement details.

Compound	**$(tBuTPA\text{-}PBI)_2CuBr_2$**	**$(tBuTPA\text{-}IMAC)_2CuBr_2$**	**$(HMAT\text{-}IMAC)_2CuBr_2$**
Formula	$C_{114}H_{114.7}Br_2CuN_6O_{0.35}$	$C_{90}H_{92}Br_2CuN_6$	$C_{98}H_{90}Br_2CuN_6$
$D_{calc.}$/ g cm^{-3}	1.252	1.133	1.359
μ/mm^{-1}	1.119	1.216	2.025
Formula Weight	1797.77	1481.05	1575.11
Colour	brown	brown	brown
Shape	tablet	prism	tablet
Size/mm^3	0.18×0.15×0.06	0.28×0.09×0.05	0.17×0.16×0.06
T/K	120(2)	110(2)	110(2)
Crystal System	triclinic	triclinic	triclinic
Space Group	P-1	P-1	P-1
a/Å	10.0664(5)	12.0933(16)	11.6745(4)
b/Å	13.6796(9)	12.3626(16)	12.3767(4)
c/Å	17.6000(9)	16.665(2)	28.6479(9)
α/°	83.395(2)	77.350(4)	82.965(2)
β/°	83.856(2)	71.246(4)	82.068(2)
γ/°	84.458(2)	67.770(4)	70.418(2)
V/Å^3	2385.0(2)	2170.3(5)	3849.8(2)
Z	1	1	2
Z'	0.5	0.5	1
Wavelength/Å	0.71073	0.71073	1.54178
Radiation type	MoK_α	MoK_α	CuK_α
Θ_{min}/°	1.504	1.791	1.562
Θ_{max}/°	29.784	26.464	68.442
Measured Refl.	51254	46110	14016
Independent Refl.	13531	8939	14016
Reflections with I > 2(I)	10091	7336	12044
R_{int}	0.0470	0.0270	0.071
Parameters	575	487	983
Restraints	0	0	0
Largest Peak	0.628	0.409	0.862
Deepest Hole	-0.404	-0.810	-0.637
GooF	1.033	1.031	1.038
wR_2 (all data)	0.1074	0.0825	0.1288
wR_2	0.0976	0.0775	0.1244
R_1 (all data)	0.0650	0.0432	0.0522
R_1	0.0412	0.0315	0.0458

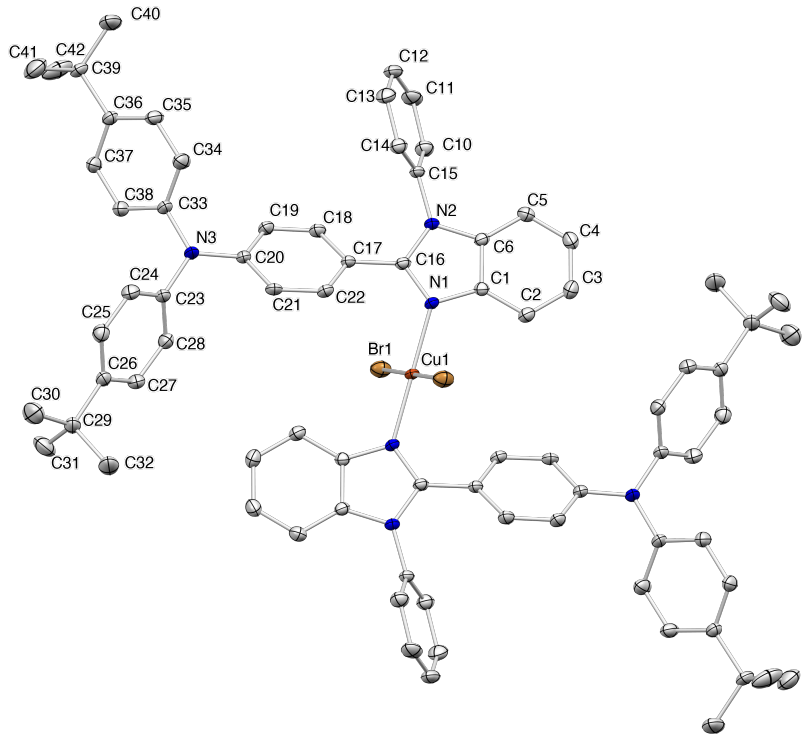


Figure S14 Solid-state structure of **(tBuTPA-PBI)$_2$CuBr$_2$**, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent benzene molecules removed for clarity. Selected bond lengths (Å): Cu1–N1 1.9518(14), N1–C16 1.322(2), N3–C20 1.404(2). Selected angles (°): N1–Cu1–Br1 90.11(4). Selected torsion angles (°): N1–C16–C17–C18 150.39(18), C16–N2–C15–C10 125.9(2).

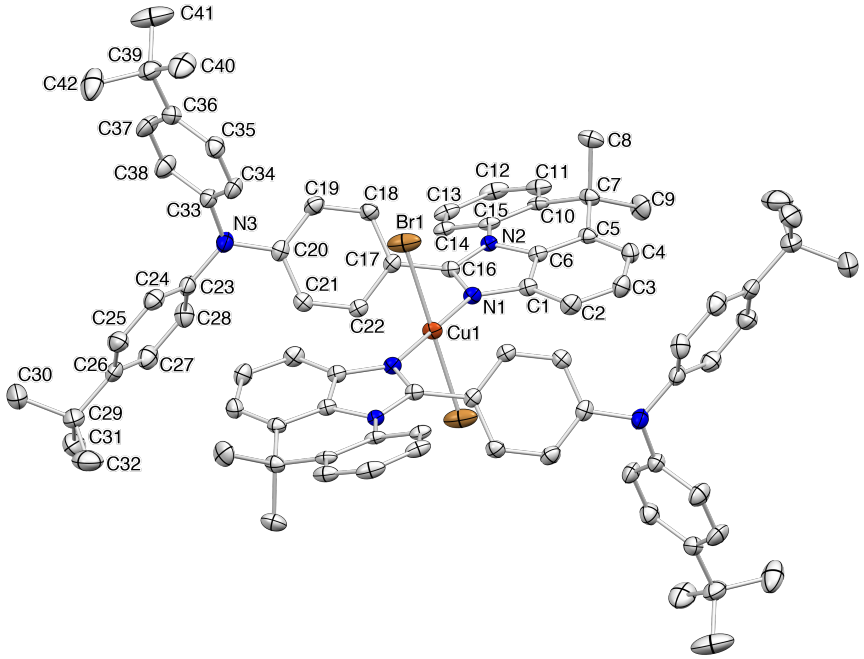


Figure S15 Solid-state structure of **(tBuTPA-IMAC)$_2$CuBr$_2$**, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent benzene molecules removed for clarity. Selected bond lengths (Å): Cu1–N1 1.9751(13), N1–C16 1.329(2), N3–C20 1.406(2). Selected angles (°): N1–Cu1–Br1 89.55(4). Selected torsion angles (°): N1–C16–C17–C18 121.06(19), C16–N2–C15–C10 125.9(2).

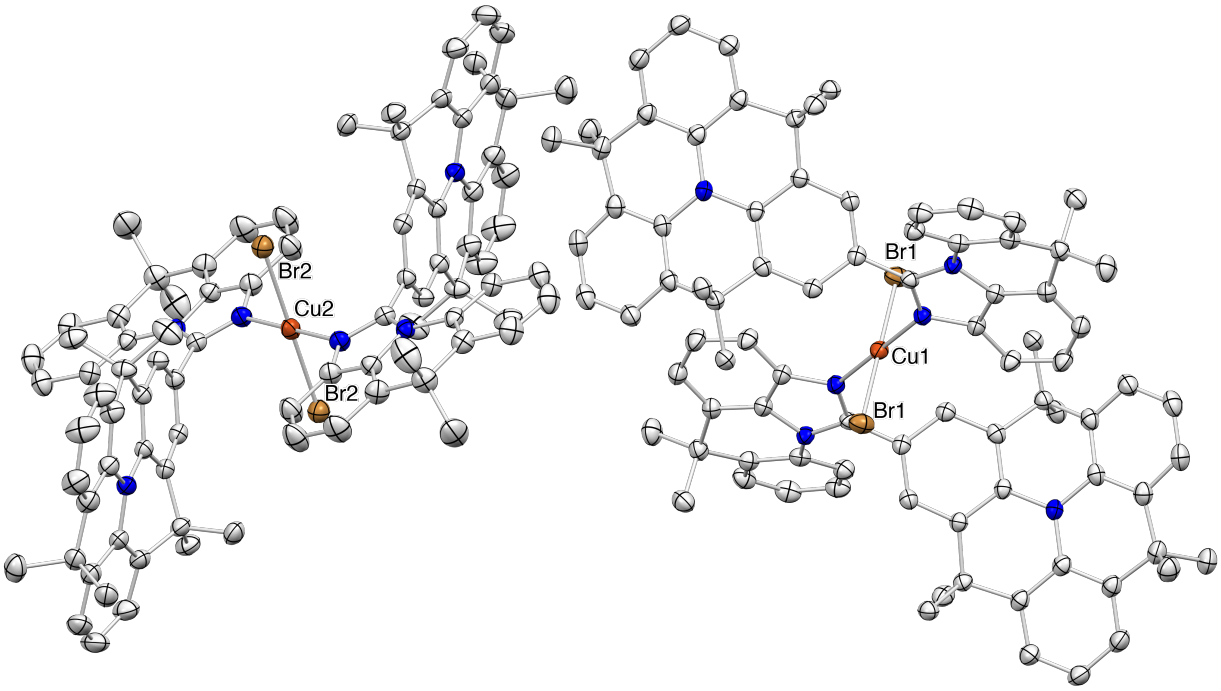


Figure S16 Solid-state structure of **(HMAT-IMAC)$_2$CuBr$_2$**, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent benzene molecules removed for clarity.

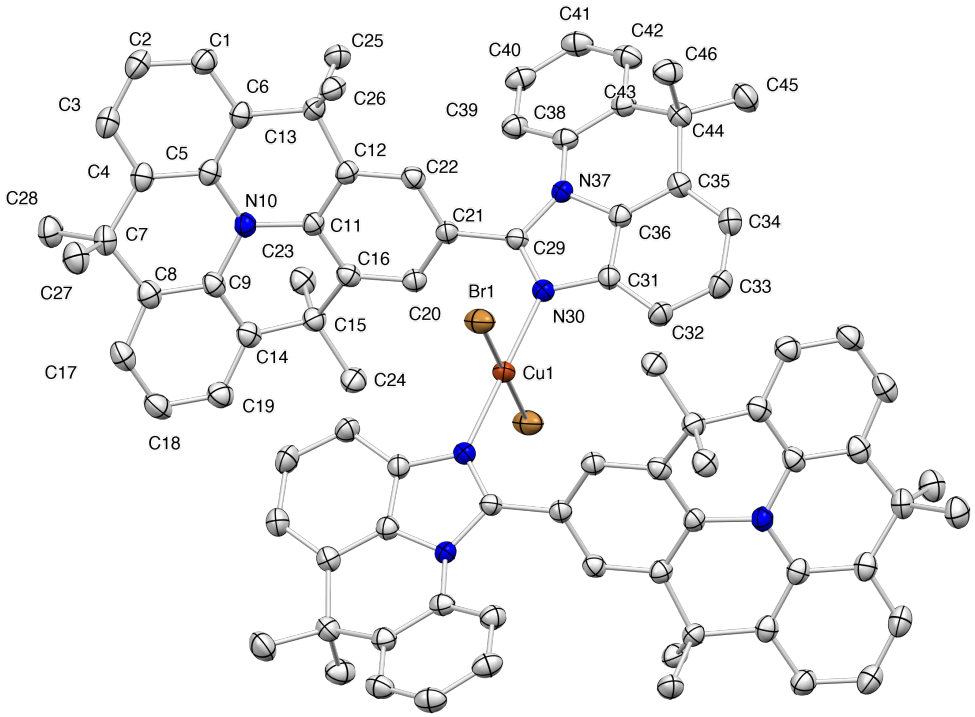


Figure S17 Solid-state structure of the first **(HMAT-IMAC)$_2$CuBr$_2$** conformation, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent benzene molecules removed for clarity.

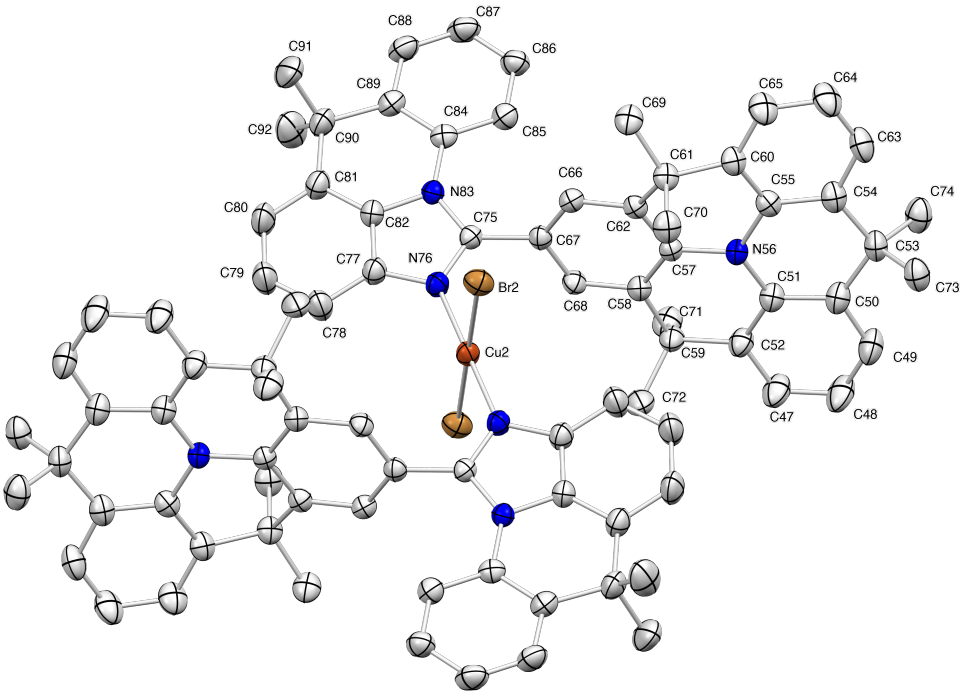


Figure S18 Solid-state structure of the second **(HMAT-IMAC)$_2$CuBr$_2$** conformation, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent molecules removed for clarity.

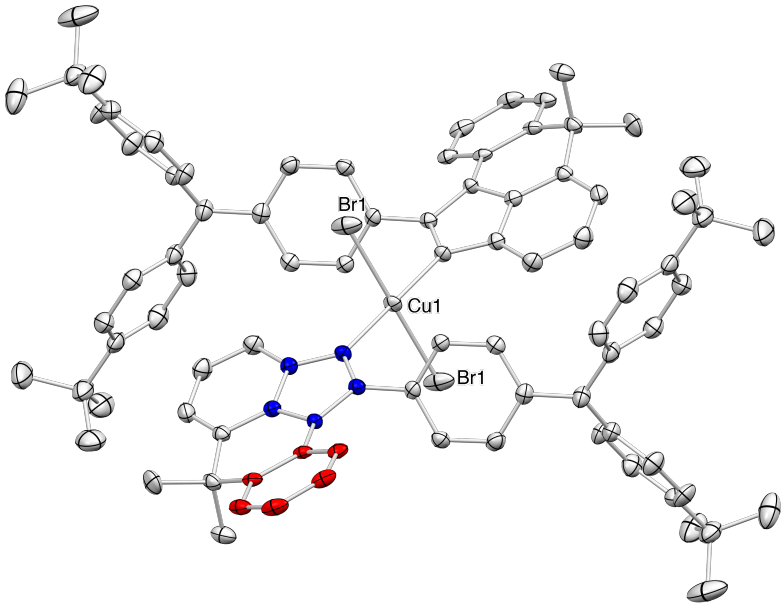


Figure S19 Solid-state structure of **(tBuTPA-IMAC)$_2$CuBr$_2$**, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent molecules removed for clarity. The dihedral angle (°) between the aryl portion depicted in red and blue is 21.57.

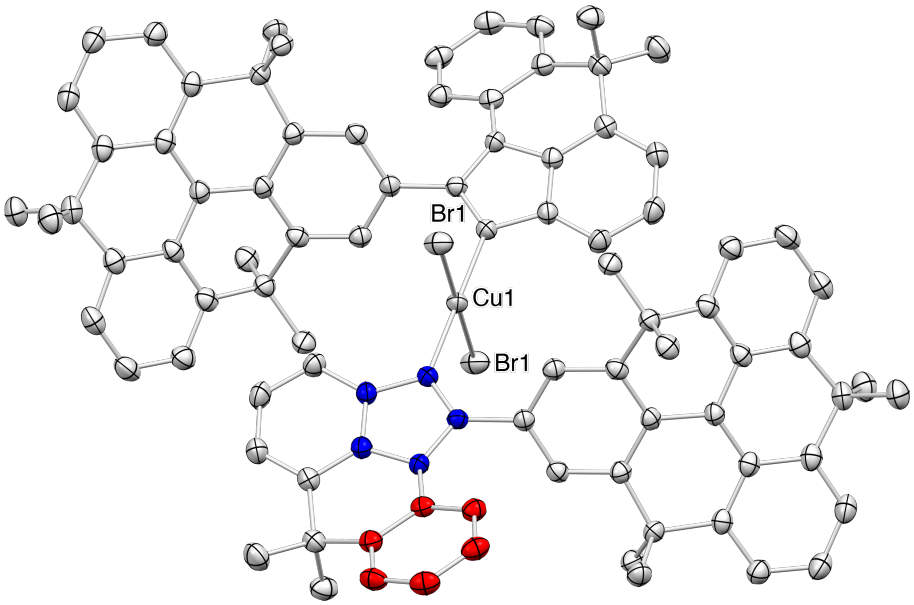


Figure S20 Solid-state structure of the first **(HMAT-IMAC)$_2$CuBr$_2$** conformation, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent molecules removed for clarity. The dihedral angle (°) between the aryl portion depicted in red and blue is 24.86.

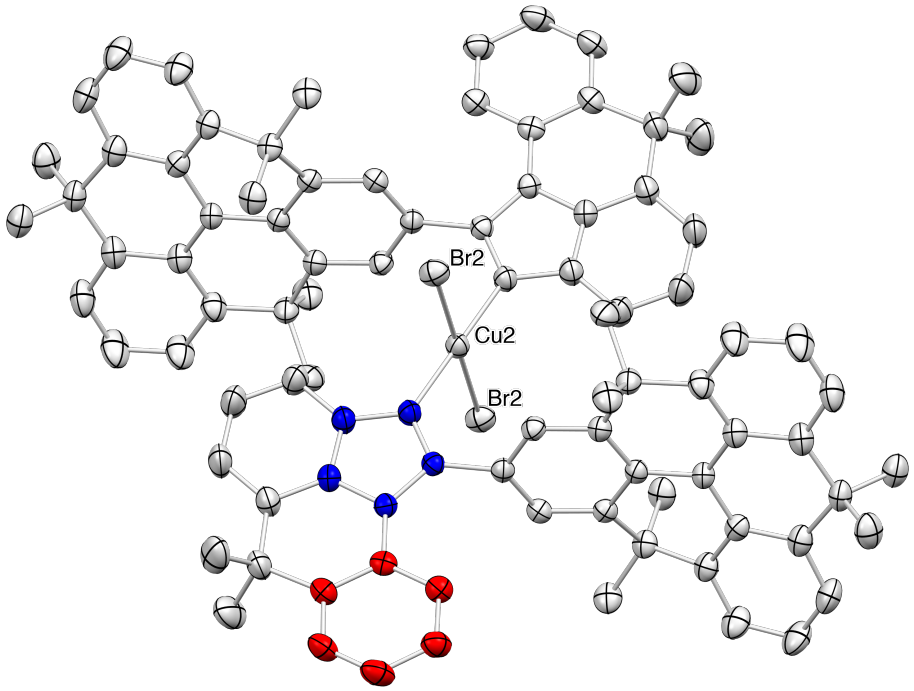


Figure S21 Solid-state structure of the second **(HMAT-IMAC)$_2$CuBr$_2$** conformation, depicted with 50 % thermal ellipsoids. Hydrogen atoms and solvent molecules removed for clarity. The dihedral angle (°) between the aryl portion depicted in red and blue is 6.91.

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