Electronic Supplementary Information

Charge-Transfer Crystal with Segregated Packing Structure Constructed with Hexaarylbenzene and Tetracyanoquinodimethane

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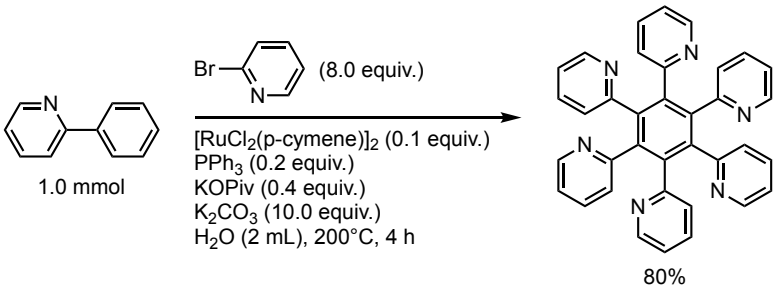
Contents

1. General

All commercially available reagents and solvents are reagent grade and were used without further purification unless otherwise noted. Solvents for the synthesis were purchased from commercial suppliers, degassed by three freeze-pump-thaw cycles, and further dried over molecular sieves (4 Å). NMR spectra were recorded on a JEOL JNM-ECX400P, JNM-ECS400 (^{1}H: 400 MHz; ^{13}C: 99.5 MHz), or a Bruker AVANCE III 500 MHz spectrometer (^{1}H: 500 MHz; ^{13}C: 125 MHz) using tetramethylsilane and $CDCl_3$ as internal standards, respectively. Photographs were obtained using Olympus BX51 or SZX7 microscopes with Olympus DP72, Nikon D5100 digital cameras. Cyclic voltammetry experiments were performed using Electrochemical Analyzer Model 660E from CH Instruments, Inc.

2. Synthesis

2.1. Synthesis of hexa(2-pyirdyl)benzene[1]



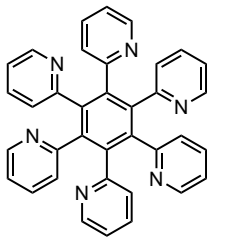
A powder of $[RuCl_2(p\text{-cymene})]_2$ (0.061 g, 0.1 mmol), PPh_3 (0.052 g, 0.2 mmol), KOPiv (0.056 g, 0.4 mmol) and K_2CO_3 (1.060 g, 10.0 mmol) were add into Microwave Vials. The vial was connected to vacuum/nitrogen manifold through a rubber tube. It was evacuated and then backfilled with nitrogen. This process was repeated three times. 2-pyridylbenzene (0.155 g, 142 μL, 1.0 mmol) and 2-bromopyridine (1.264 g, 775 μL, 8.0 mmol) were added follow to H_2O (2.0 ml) was then added. The suspended H_2O solution was bubbled by argon gas for 3 min and heated at 200°C with microwave irradiation for 4 h. The reaction mixture was then cooled to room temperature and diluted with DCM and H_2O. The product was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and removed *in vacuo*. The crude product was washed with acetone. Further purification by recrystallization using $CHCl_3$/Hexane gave pale yellow solid. (0.433 g, 0.8 mmol, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.76–6.79 (ddd, J = 7.60, 4.80, 0.90 Hz, 6H), 6.97–6.99 (d, J = 8.00 Hz, 6H), 7.19–7.24 (td, J = 8.00, 2.00 Hz, 6H), 8.14–8.15 (ddd, J = 5.20 2.00, 0.80 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 120.5 (*C*H), 127.0 (*C*H), 134.6 (*C*H), 140.3 (*C*), 148.1 (*C*H), 158.5 (*C*).

3. Crystal preparation

To a 2 ml vial, hexaarylbenzene (HAB) (0.02 mmol) and TCNQ (4.1 mg, 0.02 mmol) were dissolved in solvent (1.5 ml) or added another solvent carefully to make two layers. The obtained solution was placed in a refrigerator and the solvent was slowly evaporate or diffusion.

Table S1 CT Crystal preparation of each HAB compound

entry	HAB	solvent	result
1	**1**	Chloroform-Hexane	Mixture of each crystal
2	**1**	Chloroform-MeOH	Mixture of each crystal
3	**1**	Acetonitrile	Mixture of each crystal
4	**1**	Dichloromethane	Blue powder
5	**1**	**Chloroform**	**Dark blue crystal**
6	**2**	Chloroform-Hexane	Mixture of each crystal
7	**2**	Chloroform-MeOH	Mixture of each crystal
8	**2**	Acetonitrile	Mixture of each crystal
9	**2**	Chloroform	Blue crystal-like fiber



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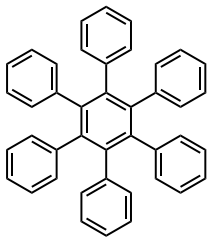

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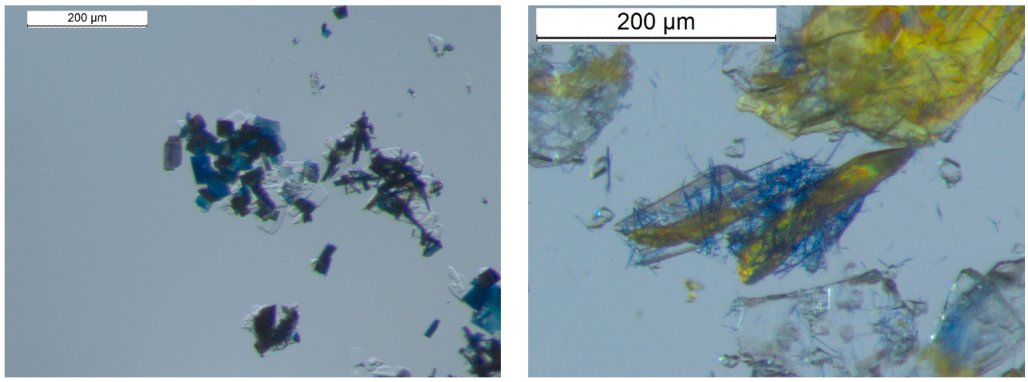

Figure S1. Crystal image of entry 3 (left) and 9 (right)

We also tried using hexaphenylbenzene to make CT crystal. Entry 9 gave a little amount of blue crystal-like fiber but its size was not suitable for single-crystal X-ray analysis.

4. Data for Single-Crystal X-Ray Structural Analyses

Single-crystal X-ray structural analyses were carried out on a Rigaku XtaLAB PRO MM007 diffractometer using graphite monochromated Cu-K_α radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for refinement, which was performed using SHELXL-2013[2].

Table S2 Summary of X-ray crystallographic data of the crystal.

CCDC Number	2076417	2099513
Empirical Formula	$C_{78}H_{38}N_{20}$	$C_{78}H_{38}N_{20}$
Formula Weight	1255.28	1255.28
Crystal System	triclinic	triclinic
Crystal Size / mm	0.3×0.3×0.01	0.2×0.2×0.01
a / Å	7.7083(2)	7.7403(0)
b / Å	17.6112(5)	17.6776(2)
c / Å	23.3347(4)	23.7797(2)
α / °	96.381(2)	96.4080(10)
β / °	96.351(2)	96.9700(10)
γ / °	94.418(2)	94.6330(10)
V / Å^3	3115.97(13)	3194.84(6)
Space Group	P/1	P/1
Z value	2	4
D_{calc} / g cm^{-3}	1.338	1.305
Temperature / K	123	293
$2\theta_{max}$ / °	151.142	150.788
μ(Cu K_α) / cm^{-1}	6.74	6.57
No. of Reflections	Total: 37815 Unique: 12448 R_{int} = 0.0431	Total: 41505 Unique: 12782 R_{int} = 0.0235
R_1[a]	0.0640	0.0801
wR_2[b]	0.2055	0.1940
GOF[c]	1.028	1.069
Max./Mini. Peak I[d] / Å^3	0.28 e$^-$/−0.31 e$^-$	0.25 e$^-$/−0.32 e$^-$

[a]:$I > 2.00\sigma(I)$. [b]:All reflections. [c]:Goodness of Fit Indicator. [d]: in Final Diff. Map.

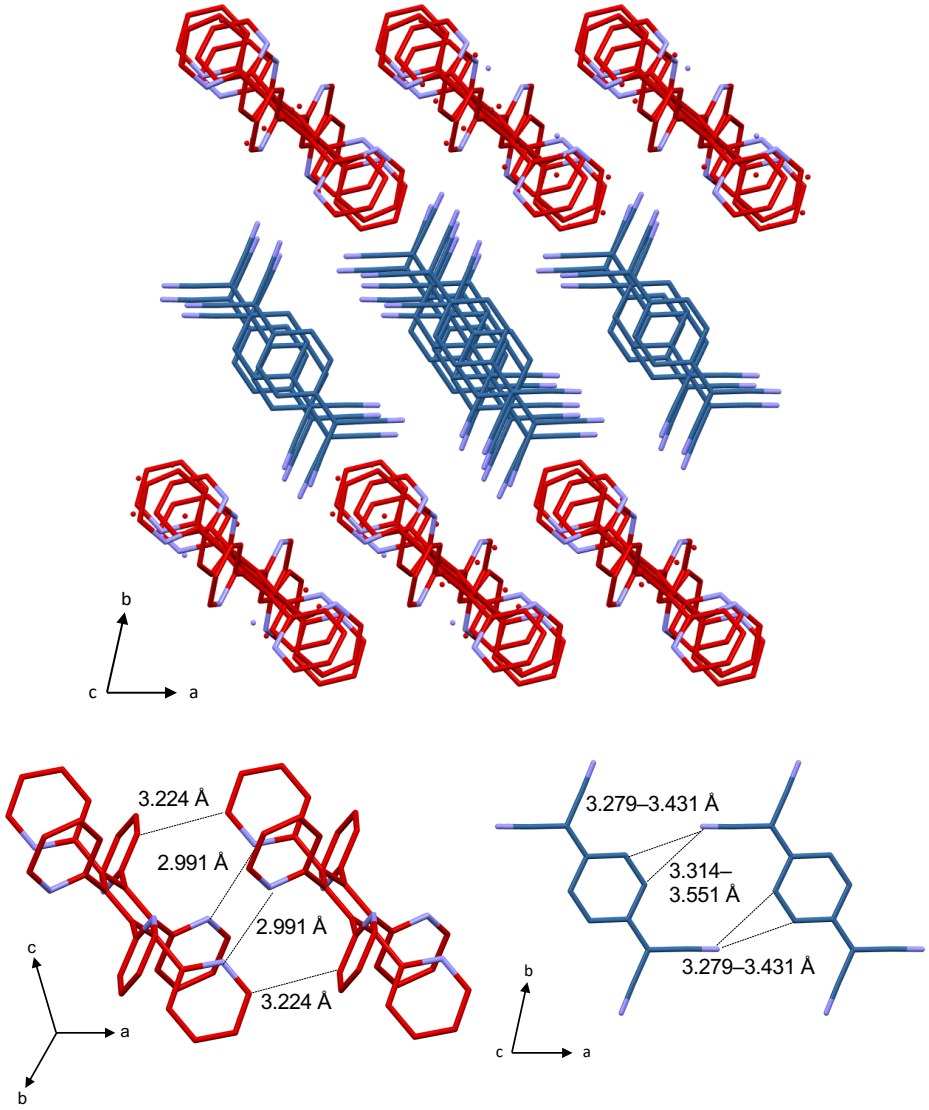

Figure S2. Crystal srtucture of CT crystal at 123 K.

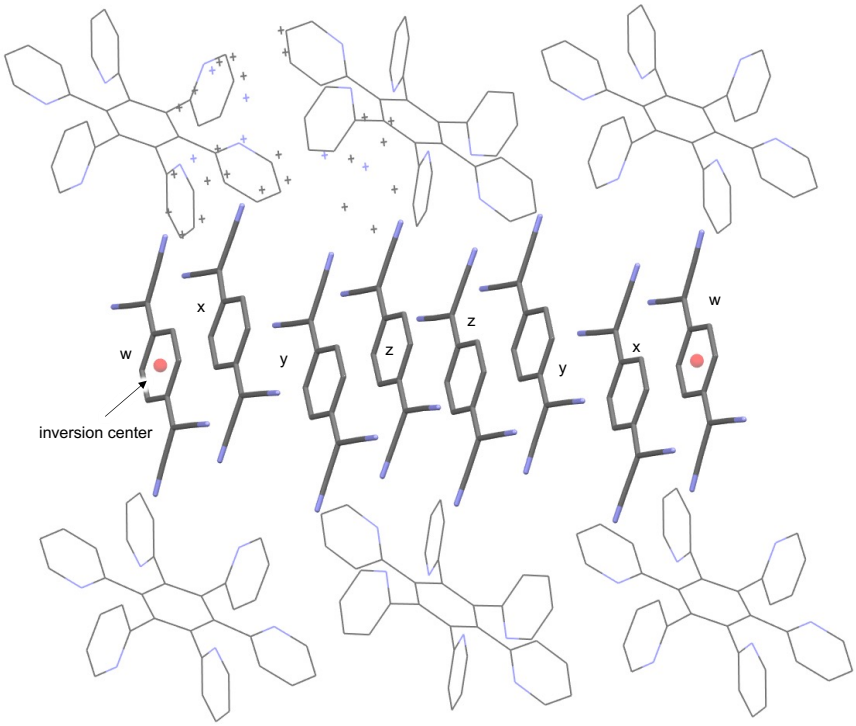

Figure S3. Crystal structure of CT crystal at 123 K indicates the inversion center on w.

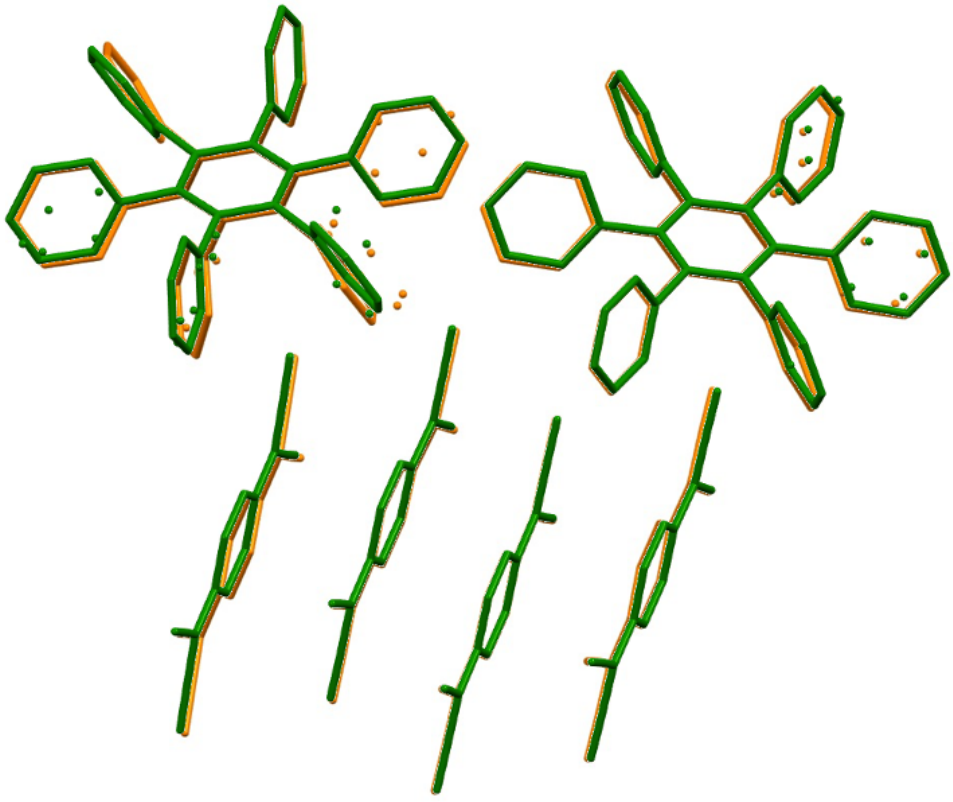

Figure S4. Crystal structure of CT crystal at 123 K (green) and 293 K (orange). There is no structure change.

5. Calculated Degree of Charge Transfer

Table S3. Bond lengths and degree of charge-transfer ρ of TCNQ in the CT crystal at 293 K.

	a / Å	b / Å	c / Å	d / Å	ρ
w	1.340	1.438	1.383	1.429	0.261
x	1.348	1.428	1.395	1.421	0.622
y	1.343	1.437	1.380	1.428	0.277
z	1.347	1.427	1.404	1.421	0.703
Avg	1.345	1.433	1.391	1.425	0.466

Table S4. Estimated degree of charge-transfer of CT crystal at 123 and 293 K using several equations.

		ρ	ρ'	ρ''
123 K	w	0.460	0.423	0.415
	x	0.674	0.658	0.595
	y	0.352	0.307	0.300
	z	0.857	0.864	0.794
	Avg	0.585	0.563	0.526
293 K	w	0.261	0.230	0.184
	x	0.622	0.551	0.494
	y	0.277	0.199	0.200
	z	0.703	0.696	0.569
	Avg	0.466	0.419	0.361

The ρ values were calculated by using the equation. $\rho = (\alpha_{CT}–\alpha_0)/(\alpha_{–1}–\alpha_0)$, α = c/(b+d). ρ' = 1–7.25(b–c)+8.07(c–d).[3] ρ'' = 23.81(a+c)/(b+d)–22.43.[4]

6. DFT Calculation

All geometry optimizations and thermal energy correction calculations (frequency analyses) using density functional theory (DFT) were performed with Gaussian 16 programs[5]. The initial geometry of CT complex was taken from the crystal structures and evaluated the energy using DFT calculation with B3LYP/6-31G level. The molecular structure was optimized using DFT calculation with ωB97X-D/Def2-TZVP.

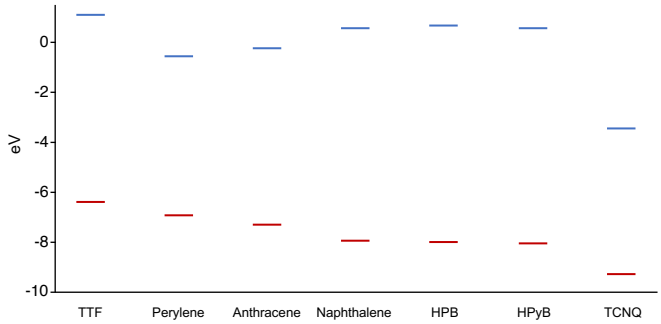

Figure S5. Energy diagram of calculated HOMO (red line) and LUMO (blue line) for each molecule.

Table S5. HOMO and LUMO energy of each donor molecule.

Donor molecule	Theoretical HOMO energy in vacuum (eV)	Theoretical LUMO energy in vacuum (eV)	HOMO energy based on UPS (eV)[6]	HOMO energy based on CV (eV)
TTF	–6.417	1.125	–5.0	–5.14[7*]
Perylene	–6.958	–0.565	–5.2	–5.48[7]
Anthracene	–7.307	–0.222	–5.7	–5.76[7]
Naphthalene	–7.975	0.540	–6.4	–6.25[7]
HPB	–7.983	0.707	No data	No data
HPyB	–8.057	0.548	No data	–5.99/–6.425
TCNQ	–9.282	–3.446	–7.4	No data

Calculated HOMO and LUMO energy were evaluated by using DFT calculations with ωB97X-D/Def2-TZVP level. Experimental HOMO energy was evaluated by ultraviolet photoelectron spectroscopy (UPS)[6] and cyclic voltammetry (CV)[7]. The experimental HOMO energy of CV was calculated by using HOMO energy of ferrocene (–4.8 eV) and equation (E_{HOMO} = –4.8 –E_{ox})[8]. E_{ox} is the oxidation potential obtained from CV measurement. * The TTF HOMO energy was calculated by using literature data[7].

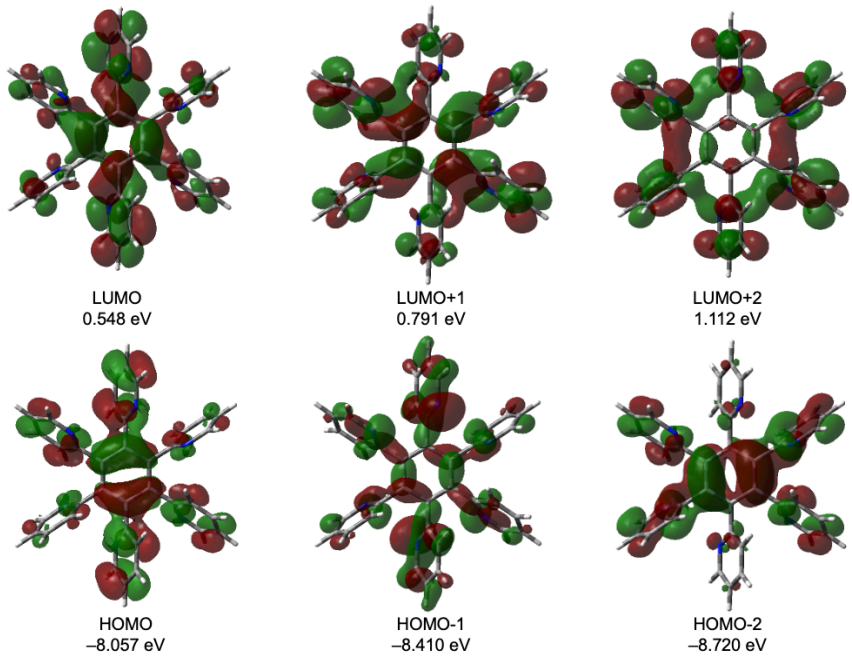

Figure S6. Molecular orbitals ranging from HOMO–2 to LUMO+2 of HPyB.

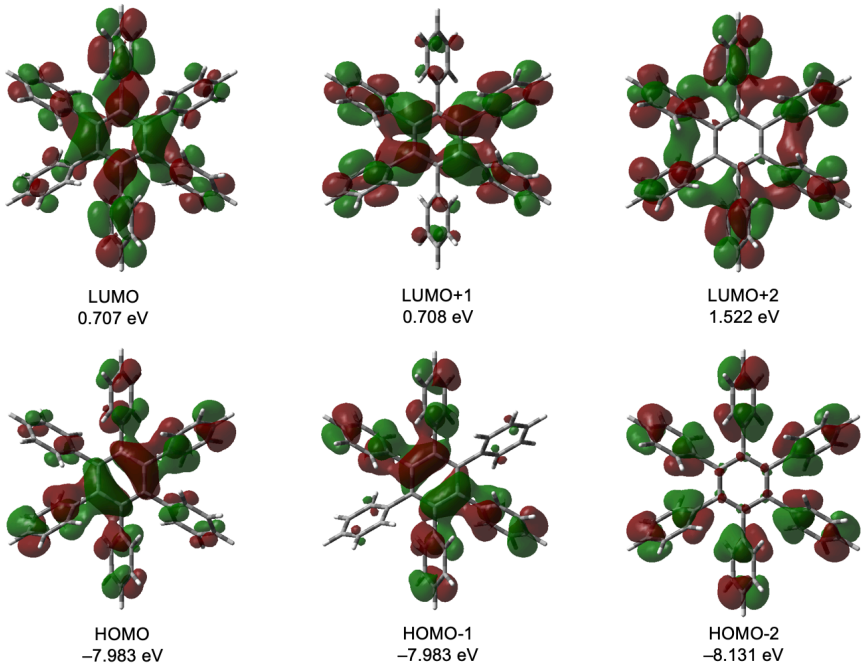

Figure S6. Molecular orbitals ranging from HOMO–2 to LUMO+2 of HPB.

7. Cyclic Voltammetry Study of HPyB

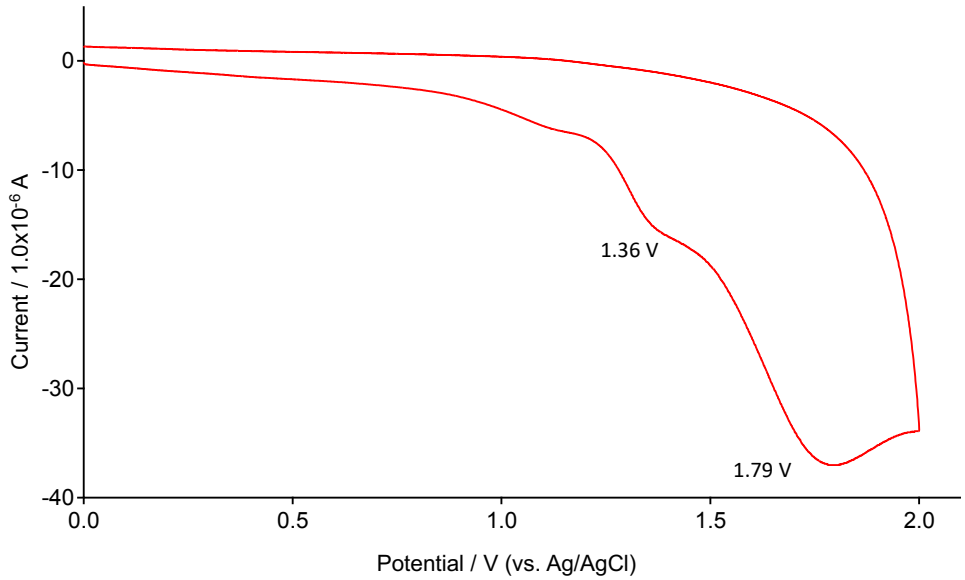

Figure S7. Cyclic volutammogram of HPyB. The measurement was performed in CH_2Cl_2 ([HPyB] = 5.0 mM, $[(NBu_4)PF_6]$ = 0.10 M) with a $AgNO_3$ electrode as the reference electrode. After measurement, feroccene was added as internal standard.

8. References

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9. NMR Spectra

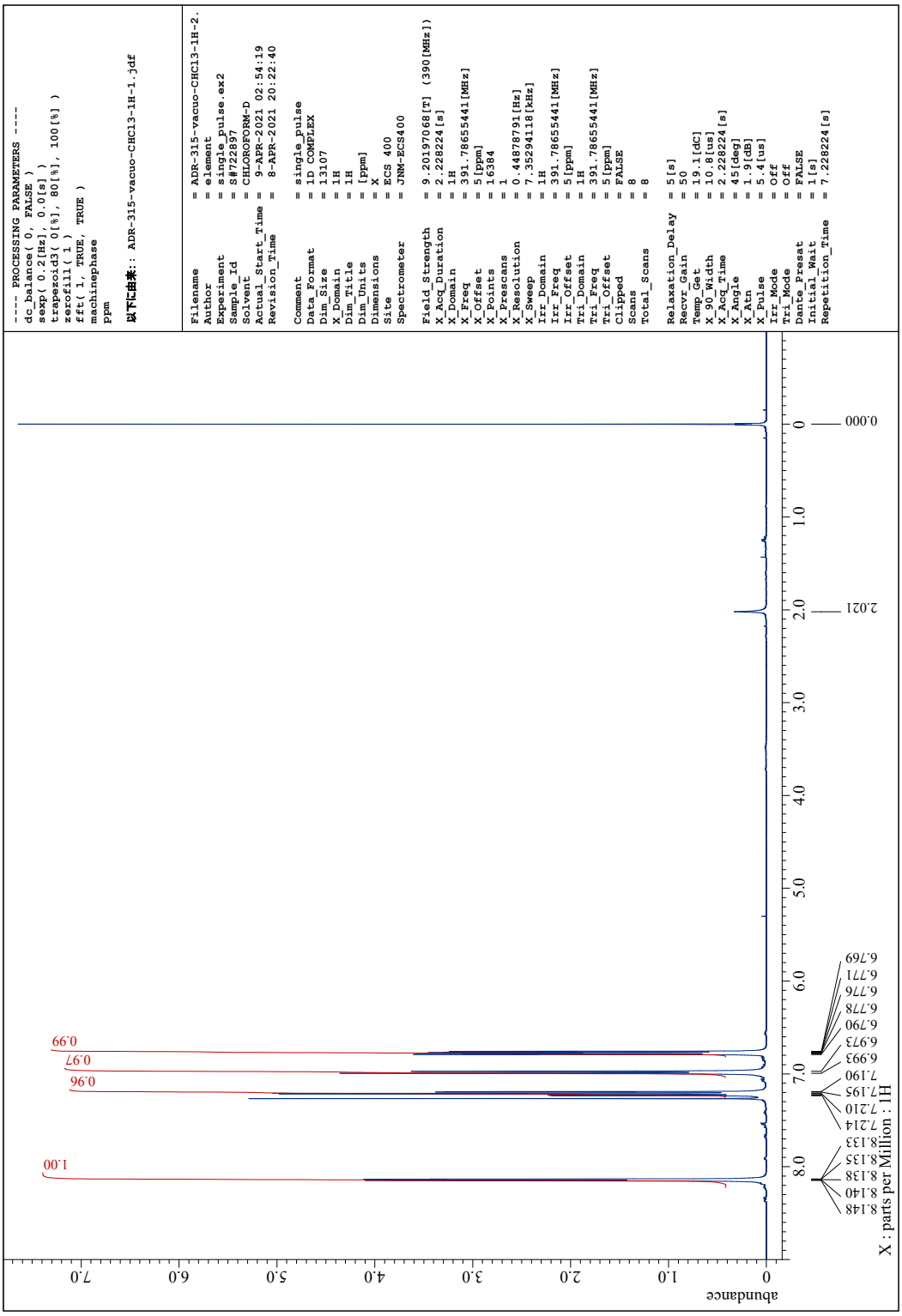

Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of hexa(2-pyirdyl)benzene.

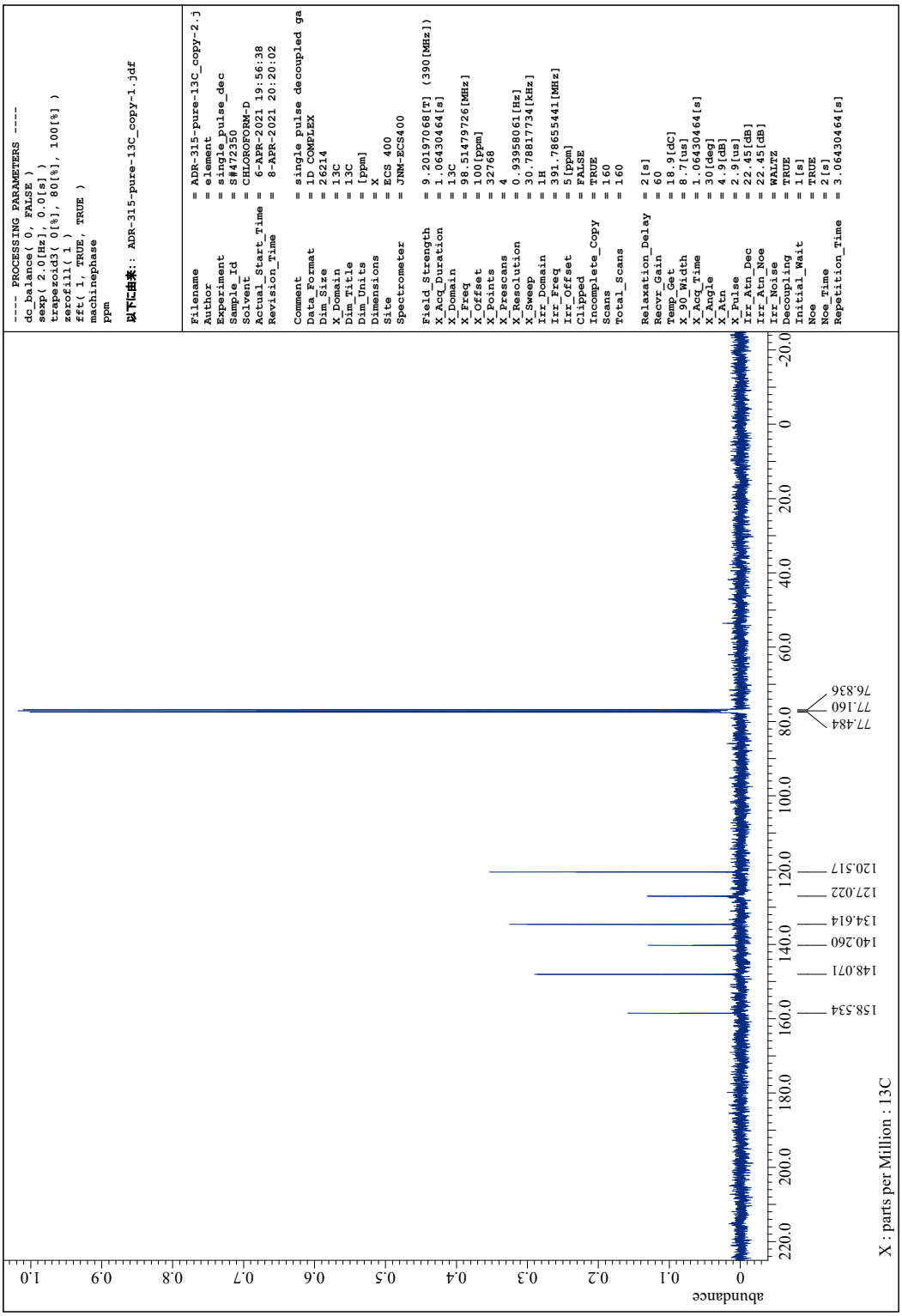

Figure S9. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of hexa(2-pyirdyl)benzene.