

Supporting Information

For

Triphenylene-based tris-*N*-heterocyclic stannylenes

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General Information:

Air and moisture sensitive procedures are conducted under N₂ atmosphere using standard Schlenk techniques or inside a glove box. Toluene and hexane were degassed and then dried by passing through a molecular sieves packed column under nitrogen. C₆D₆ was dried with Na/K alloy and distilled under N₂ atmosphere. Hexaiminetriphenylene,¹ **1b**,² and Sn[N(TMS)₂]₂ were prepared according to the reported procedures.³ ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were recorded using Bruker AVIII 400 MHz NMR spectrometer. The ¹H and ¹³C chemical shifts are reported in ppm (δ) with respect to the signal of solvent residual. Tetramethylstannane (δ = 0 ppm) was used as the standard for ¹¹⁹Sn NMR spectrum. UV-vis spectra were recorded with Ocean Optics USB4H05427 spectrometer. Elemental analysis was performed on a Heraeus varioIII-NCH elemental analyzer.

X-ray Crystallography:

Diffraction data of **2a** was collected at T = 150(2) K with a Bruker AXS APEX CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Cell parameters were retrieved and refined using DENZO-SMN software on all reflections. Data reduction was performed with DENZO-SMN software. Structural analysis was conducted with SHELXTL, and the structure was solved and refined using SHELXL-97 by full-matrix least-squares on F² values. Hydrogen atoms were added to the structure models in calculated positions. Due to the disorder of solvent molecules, several restraints are applied for structural refinement. Isotropic restraint is applied to the inclusion toluene molecules and a phenyl ring (C86-C90) of **2a**. Distance and isotropic restraints are used for the hexane molecule. The rigid-bond restraints are applied to C94 and C95. The distance restraint is also used for a phenyl ring (C39-C44) of **2a** and three of the inclusion toluene molecules. Crystallographic data of **2a** has been deposited at the Cambridge Crystallographic Data Center with deposition number of CCDC-1049534, and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

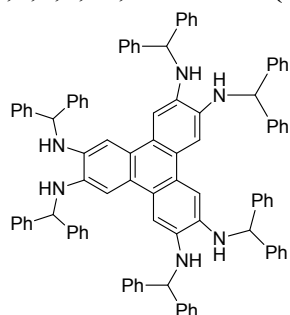
¹ L. Chen, J. Kim, T. Ishizuka, Y. Honsho, A. Saeki, S. Seki, H. Ihee, D. Jiang, *J. Am. Chem. Soc.*, 2009, **131**, 7287

² Y.-T. Wang, M.-T. Chang, G.-H. Lee, S.-M. Peng, C.-W. Chiu, *Chem. Commun.*, 2013, **49**, 7258

³ D. H. Harris, M. F. Lappert, *J. Chem. Soc. Chem. Commun.*, 1974, 895

Synthesis:

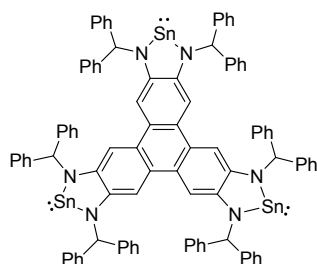
2,3,6,7,10,11-hexakis(*N*-benzhydrylamine)triphenylene (1a**)** : An ether solution (10 mL)



of hexaiminetriphenylene (560 mg, 0.43 mmol) was added slowly into an ether suspension (10 mL) of lithium aluminium hydride (120 mg, 3.24 mmol) at room temperature. The resulting mixture was allowed to stir for overnight. After reaction, the reaction was quenched with cold water and ether. Light yellow compound **1a** was insoluble in both ether and water, and was collected by filtration (424 mg, yield: 75 %). ¹H NMR (CDCl₃, 400 MHz, ppm):

δ 7.26~7.38 (m, 60 H, Ph), 7.08 (s, 6 H, triphenylene), 5.48 (s, 6 H, *CHPh*₂), 4.04 (s, 6 H, *NH*). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 143.1 (CN, triphenylene), 135.2 (*ipso-C*, Ph), 128.7 (CH, Ph), 127.5 (CH, Ph), 127.3 (CH, Ph), 122.2 (triphenylene), 106.9 (CH, triphenylene), 63.0 (*CHPh*₂). Anal. Calcd. for C₉₂H₇₈N₆: C, 87.17; H, 6.20; N, 6.63. Found: C, 87.39; H, 5.82; N, 5.74.

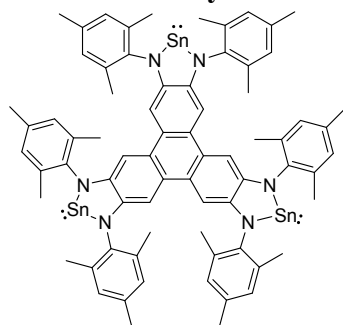
Tris-*N*-heterocyclic stannylene **2a**: Hexamine **1a** (100 mg, 0.079 mmol) and Sn[N(TMS)₂]₂



(170 mg, 0.387 mmol) were mixed in 40 mL of toluene. The reaction mixture was heated for 16 hours at 110 °C. After cooling to room temperature, all volatiles were removed under vacuum and the resulting solid residue was washed with hexane (5 mL, two times) to afford **2a** as dark-red solid (86 mg, yield: 65 %). ¹H NMR (C₆D₆, 400 MHz, ppm): δ 7.66 (s, 6 H, triphenylene), δ

7.28 (d, 24 H, *ortho-CH*), δ 7.08~7.11 (m, 36 H, *meta-* and *para-CH*), 6.61 (s, 6 H, *NCHPh*₂). ¹³C NMR (C₆D₆, 100 MHz, ppm): δ 146.8 (CN, triphenylene), 145.6 (*ipso-C*, Ph), 129.5 (CH, Ph), 129.3 (CH, Ph), 122.9 (triphenylene), 105.9 (CH, triphenylene), 66.8 (*NCHPh*₂) ¹¹⁹Sn NMR (C₆D₆, 149.16 MHz, ppm): δ 226.4 ppm. Anal. Calcd. for C₉₆H₇₂N₆Sn₃: C, 69.22; H, 4.36; N, 5.05. Found: C, 68.80; H, 4.76; N, 5.14. Compound **2a** turns black at temperature higher than 330 °C.

Tris-*N*-heterocyclic stannylene **2b**: Hexamine **1b** (100 mg, 0.097 mmol) and Sn[N(TMS)₂]₂



(210 mg, 0.477 mmol) were mixed in 40 mL of toluene. The reaction mixture was heated at 110 °C for 16 hours. After reaction, all volatiles were removed under vacuum to yield dark-red solid, which was then washed with hexane (5 mL, two times) to afford 97 mg of **2b** (yield: 72 %). ¹H NMR (C₆D₆, 400 MHz, ppm): δ 7.36 (s, 6 H, triphenylene), 7.04 (s, 12 H, Mes), 2.53 (s,

18 H, *p*-Me), 2.03 (s, 36 H, *o*-Me). ^{13}C NMR (C_6D_6 , 100 MHz, ppm): δ 143.9 (*ipso*-C, Mes), 141.5 (CN, triphenylene), 134.5 (*ortho*-C, Mes), 133.9 (*para*-C, Mes), 129.1 (CH, Mes), 123.5 (triphenylene), 104.1 (CH, triphenylene), 21.2 (*p*-Me), 17.9 (*o*-Me). ^{119}Sn NMR (C_6D_6 , 149.16 MHz, ppm): δ 257.1 ppm. Anal. Calcd. for $\text{C}_{72}\text{H}_{72}\text{N}_6\text{Sn}_3$: C, 62.78; H, 5.27; N, 6.10. Found: C, 63.67; H, 5.80; N, 6.42. Compound **2b** starts to decompose at 385°C.

UV-vis Spectrometry:

Electronic absorption studies were carried out with Ocean Optics USB4H05427 spectrometer. Samples with concentration of 1×10^{-4} M were prepared in a glove-box and were transferred to a glass-stopper sealed cuvette for absorbance measurement.

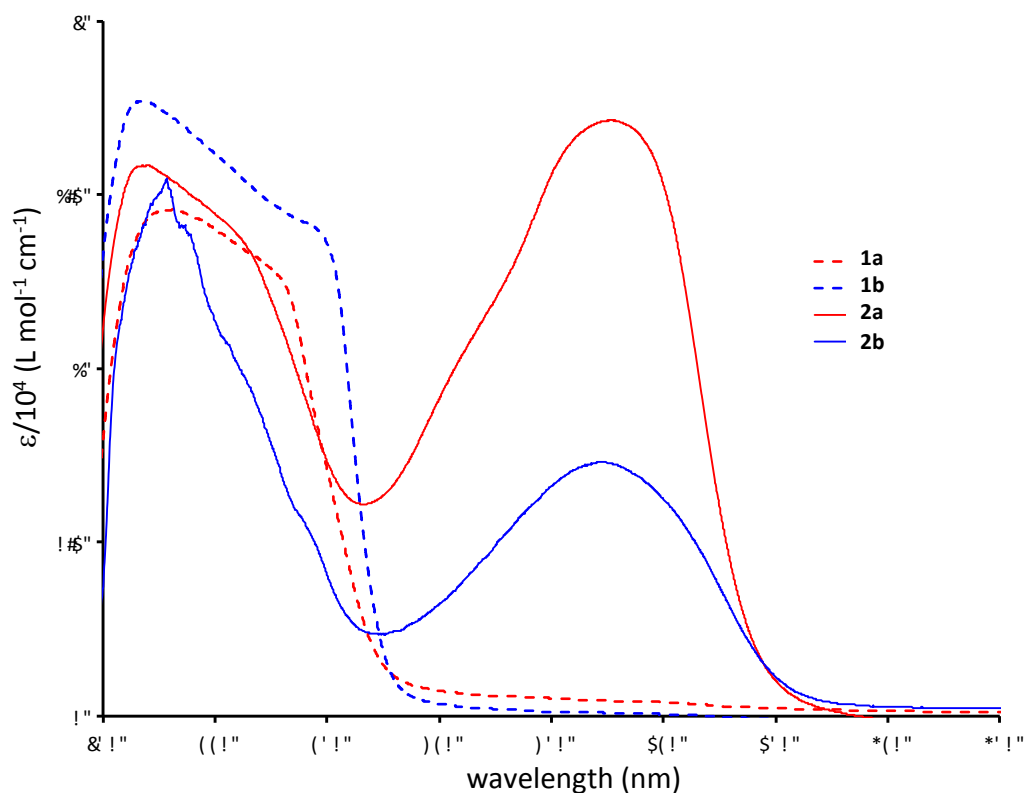


Figure S1: UV-vis absorption spectra of **1a**, **1b**, **2a**, and **2b** in toluene.

Table S1. Crystal data and structure refinement for ic16333. **(2a)**

Identification code	ic16333
Empirical formula	C ₁₄₈ H ₁₃₅ N ₆ Sn ₃
Formula weight	2353.69
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.4902(3) Å α = 85.9683(10)°. b = 17.8054(4) Å β = 84.8475(10)°. c = 32.1772(7) Å γ = 88.9623(9)°.
Volume	5970.6(3) Å ³
Z	2
Density (calculated)	1.309 Mg/m ³
Absorption coefficient	0.678 mm ⁻¹
F(000)	2430
Crystal size	0.45 x 0.16 x 0.15 mm ³
Theta range for data collection	1.15 to 25.00°.
Index ranges	-12 ≤ h ≤ 12, -21 ≤ k ≤ 21, -34 ≤ l ≤ 38
Reflections collected	54319
Independent reflections	20824 [R(int) = 0.0596]
Completeness to theta = 25.00°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.908 and 0.755
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	20824 / 332 / 1380
Goodness-of-fit on F ²	1.019
Final R indices [I > 2σ(I)]	R1 = 0.0623, wR2 = 0.1744
R indices (all data)	R1 = 0.1085, wR2 = 0.2059
Largest diff. peak and hole	1.196 and -0.961 e.