## Supporting Information

# Noncovalently Netted, Photoconductive Sheets with Extremely High Carrier Mobility and Conduction Anisotropy from Triphenylene-Fused Metal Trigon Conjugates 

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## Section 1. Materials and Methods

2,3,6,7,10,11-hexabromo-triphenylene $\mathbf{2},{ }^{[S 1]}$ and 4-(dodecyloxy)-2- hydroxy-benzaldehyde ${ }^{[52]}$ were prepared according to reported methods.

Crystals were obtained with vapor diffusion method from DMSO-diethyl ether mixed solvent and the data crystal was a red prism of approximate dimensions $0.20 \times 0.20 \times 0.20 \mathrm{~mm}$ $\left(\mathrm{C}_{84} \mathrm{H}_{102} \mathrm{~N}_{6} \mathrm{O}_{17} \mathrm{Zn}_{3} \mathrm{~S}_{11}\right)$. Data were collected on a Rigaku Mercury CCD diffractometer in the scan range $\theta \leq 27.5^{\circ}$. Of the 38907 reflections collected, 7360 were unique ( $R_{\text {int }}=0.078$ ). The
structures were solved by direct methods and refined by full-matrix least square procedures. Solution and structure refinement calculations for the structure were performed using the Crystal Structure 3.8 software of Molecular Structure Corporation.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a JEOL model JNM-LA400 NMR spectrometer, where chemical shifts ( $\delta$ in ppm) were determined with a residual proton of the solvent as standard. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectroscopy was performed on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode using 9-nitroanthracene or dithranol as matrix. Electronic absorption spectra were recorded using a quartz cell of $1-\mathrm{cm}$ path length on a JASCO model V-570 spectrophotometer equipped with a temperature controller. Fluorescence spectra were recorded using a quartz cell of $1-\mathrm{cm}$ path length on a JASCO model FP-6600 spectrofluorometer equipped with a temperature controller. The samples (dispersed in PEG $(M \mathrm{w}=400)$ ) for fluorescence spectroscopy and fluorescence depolarization measurement are prepared with an absorbance of less than 0.1 at the excitation wavelength. Fluorescence quantum yields were measured by using quinine sulfate $\left(1 \mathrm{~N}_{2} \mathrm{SO}_{4}\right)$ as an external standard. Infrared (IR) spectra were recorded on a JASCO model FT IR-6100 Fourier transform infrared spectrometer. Field emission scanning electron microscopy (FE SEM) was performed on a JEOL model JSM-6700 FE-SEM operating at an accelerating voltage of 5.0 kV . Transmission electron microscope (TEM) images were obtained on a JEOL model JEM-3200 microscope. Powder x-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing the xerogel on glass substrate. Semi-empirical calculations at the AM1 level were performed on Spartan'04 (Wavefunction Inc.). Electrochemistry measurements were performed with CV on an ALS Model 610B electrochemical analyzer with a three electrodes configuration using a platinum wire as the counter electrode, a platinum disc as the working electrode ( 2 mm diameter), and a non aqueous $\mathrm{Ag} / \mathrm{Ag}^{+}$electrode ( Ag wire in $10 \mathrm{mM} \mathrm{AgNO}_{3}$ in anhydrous acetonitrile solution) as the reference electrode.

Electrical measurements were carried out at ambient temperature in air between a $10-\mu \mathrm{m}$ width Pt electrodes by a two-probe method using a Keithley model 2635 sourcemeter. Typically, $3 \mu \mathrm{~L}$ of $\mathbf{T S Z n}_{3}$ gel in decalin ( $10 \mathrm{mg} / \mathrm{mL}$ ) was homogenously drop casted onto the electrode to give a film and dried under vacuum. For iodine doping, the same $\mathbf{T S Z n}_{3}$ gel electrode was put into an iodine atmosphere for 2 h before measurement. For the sandwich structure device fabrication, $3 \mu \mathrm{~L}$ of $\mathbf{T S Z n}_{3}$ gel in decalin ( $10 \mathrm{mg} / \mathrm{mL}$ ) was homogenously spin coated onto an Al substrate to give a film with thickness around $10 \mu \mathrm{~m}$ and then over coated with 20-nm thick Au. Light irradiation was performed using an Asahi Spectra model MAX-301
xenon light source. I-V curves were recorded at bias voltages from -2.0 to 2.0 V , on irradiation from the Au electrode with visible light ( $400-700 \mathrm{~nm}$ ). Film thickness was measured by FE SEM.

Laser flash photolysis time-resolved microwave conductivity (FP TRMC) measurements were carried out at $25{ }^{\circ} \mathrm{C}$ in air, where the resonant frequency and microwave power were properly adjusted at 9.1 GHz and 3 mW , respectively. Charge carrier were photochemically generated using the nanosecond laser pulses from a Nd:YAG laser (a third harmonic generation ( $\lambda=355 \mathrm{~nm}$ ) of Spectra-Physics INDY-HG (FWHM 5-8 ns)). The power density of the laser was set at $3.4-14.7 \mathrm{mJcm}^{-2}$ pulse $^{-1}$. Transient conductivities ( $\Phi \Sigma \mu$ ) were evaluated according to an equation $\Phi \Sigma \mu=(1 / \mathrm{A})\left(\Delta P_{\mathrm{r}} / P_{\mathrm{r}}\right)$, where A and $P_{\mathrm{r}}$ are sensitivity factor and reflected microwave power, respectively. Time-of-flight transient current was measured at $25{ }^{\circ} \mathrm{C}$ by photoirradiation from with the $355-\mathrm{nm}$ pulse laser. The laser intensity was attenuated at 9.6 $\mathrm{mJcm}^{-2}$ pulse ${ }^{-1}$, while bias voltage was $2-16 \mathrm{~V}$. For the fabrication, $\mathbf{T S Z n}_{3}$ was dissolved in toluene ( $0.2 \mathrm{wt} \%$ ) and drop-casted onto an Au-interdigitated electrode with $5 \mu \mathrm{~m}$ gap to form a thin film with thickness of about $10 \mu \mathrm{~m}$.

## Section 2. Synthesis

(1) Synthesis of Triphenylene-Cored Hexamine


3: A toluene solution ( 50 mL ) of tris(dibenzylideneacetone)dipalladium( 0 ) ( $0.448 \mathrm{~g}, 0.49$ $\mathrm{mmol})$ and rac-BINAP ( $0.607 \mathrm{~g}, 0.98 \mathrm{mmol}$ ) was degassed by four freeze-pump-thaw cycles, purged with Ar , and stirred at $110^{\circ} \mathrm{C}$ for 30 min . After cooling at r.t., the mixture was added with benzophenone imine ( $2.65 \mathrm{~mL}, 15.77 \mathrm{mmol}$ ), 2,3,6,7,10,11-hexabromo-triphenylene 2 $(1.419 \mathrm{~g}, 2.02 \mathrm{mmol})$, and sodium tert-butoxide $(1.516 \mathrm{~g}, 15.77 \mathrm{mmol})$, and the mixture was stirred at $110{ }^{\circ} \mathrm{C}$ overnight. The mixture was cooled at r.t., diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, filtered through a pad of Celite, and evaporated to dryness. The residue was subjected to column chromatography on silica gel with AcOEt/hexane (1:4) as eluent. The last fraction was collected and evaporated to dryness, to give $\mathbf{3}(2.001 \mathrm{~g}, 1.53 \mathrm{mmol})$ as yellow solid in $76 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta(\mathrm{ppm}) 7.62-7.64(\mathrm{~m}, 12 \mathrm{H}, o-\mathrm{Ph} \mathrm{CH}), 7.34-7.64(\mathrm{~m}, 6 \mathrm{H}, o-\mathrm{Ph} \mathrm{CH})$, 7.27-7.30 (m, 12H, $m-\mathrm{Ph} \mathrm{CH}$ ), 7.19-7.22 (m, 6H, $o-\mathrm{Ph} \mathrm{CH}$ ), 7.12-7.15 (m, 12H, $m-\mathrm{Ph} \mathrm{CH}$ ), $7.04(\mathrm{~s}, 6 \mathrm{H}$, triphenylene $\mathrm{C} H), 6.93-6.94(\mathrm{~m}, 12 \mathrm{H}, p-\mathrm{Ph} \mathrm{CH}) .{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta(\mathrm{ppm})$ 168.2, 142.0, 140.2, 137.2, 130.8, 129.6, 129.1, 128.4, 128.2, 125.8, 114.6. MALDI-TOF MS for $\mathrm{C}_{96} \mathrm{H}_{66} \mathrm{~N}_{6}$ (calcd. 1302.53): $m / z=1303.76\left([\mathrm{M}+\mathrm{H}]^{+}, 100 \%\right)$. UV/Vis (THF): $\lambda_{\text {max }}(\mathrm{nm}) 287$, 387. IR (KBr pellet): $v\left(\mathrm{~cm}^{-1}\right) 3056,3024,1621,1597,1445,1288,956,694$. Anal. Calcd. for $\mathrm{C}_{96} \mathrm{H}_{66} \mathrm{~N}_{6}: \mathrm{C}, 88.45 ; \mathrm{H}, 5.10 ; \mathrm{N}, 6.45$. Found: C, 87.97; H, 5.40; N, 6.23\%.
4: To a THF solution ( 10 mL ) of $\mathbf{3}(0.219 \mathrm{~g}, 0.17 \mathrm{mmol})$ was added a 2.0 M aqueous HCl solution ( $0.5 \mathrm{~mL}, 1.0 \mathrm{mmol}$ ) and the mixture was stirred at r.t. for 0.5 h . The precipitate was isolated by centrifugation, washed with hexane ( $5.0 \mathrm{~mL} \times 3$ ), and dried under vacuum, to give $4(0.076 \mathrm{~g}, 0.14 \mathrm{mmol})$ as light yellow solid in $84 \%$ yield. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}$ ): $\delta(\mathrm{ppm}) 7.91$ ( $\mathrm{s}, 6 \mathrm{H}$, triphenylene CH ), 3.94 (brs, $12 \mathrm{H}, \mathrm{NH}_{2}$ ). ${ }^{13} \mathrm{C}$ NMR (DMSO- $d_{6}$ ): $\delta(\mathrm{ppm})$ 132.66, 129.55, 125.55. MALDI-TOF MS for $\mathrm{C}_{18} \mathrm{H}_{18} \mathrm{~N}_{6}$ (calcd. 318.16): $m / z=318.23\left([\mathrm{M}+\mathrm{H}]^{+}, 100 \%\right)$. UV/Vis (MeOH): $\lambda_{\text {max }}(\mathrm{nm}) 286,331$. IR (KBr pellet): $v\left(\mathrm{~cm}^{-1}\right) 3388,3332,3231,2926,2610$, 1635, 1517, 1438, 1281, 872. Anal. Calcd. for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{~N}_{6} \mathrm{Cl}_{6}$ : C, $40.25 ; \mathrm{H}, 4.50 ; \mathrm{N}, 15.65$. Found: C, 40.66; H, 4.48; N, 15.78\%.
(2) Synthesis of $\mathbf{T S H}_{6}$ and Metal Trigon $\mathbf{T S Z n}_{3}$

$\mathrm{TSH}_{6}$
$\mathrm{TSZn}_{3}$
TSH $_{6}$ : To a suspension of $4(0.067 \mathrm{~g}, 0.12 \mathrm{mmol})$ in $\mathrm{EtOH}(3.0 \mathrm{~mL})$ was added $\mathrm{Et}_{3} \mathrm{~N}(0.109 \mathrm{~g}$, $1.08 \mathrm{mmol})$. The mixture was stirred at r.t. for 10 min , added with an EtOH $(3.0 \mathrm{~mL})$ solution of 4-dodecyloxy-2-hydroxybenzaldehyde ( $0.345 \mathrm{~g}, 1.12 \mathrm{mmol}$ ), and the mixture was stirred at reflux temperature for 12 h . The resulting suspension was cooled at $-10^{\circ} \mathrm{C}$ and stirred for 1 h . The precipitate was collected by filtration, washed with cold EtOH , and dried under vacuum, to give $\mathbf{T S H}_{6}(0.234 \mathrm{~g}, 0.11 \mathrm{mmol})$ as red solid in $91 \%$ yield. ${ }^{1} \mathrm{H}$ NMR (THF- $\left.d_{8}\right): \delta(\mathrm{ppm}) 10.73$ (brs, $6 \mathrm{H}, \mathrm{OH}$ ), 8.73 (brs, $6 \mathrm{H}, \mathrm{N}=\mathrm{CH}$ ), 8.41 (brs, 6 H , triphenylene CH ), 7.25 (d, $J=8.4 \mathrm{~Hz}, 6 \mathrm{H}$, Ar-H), 6.36 (s, 6H, Ar-H), $6.33(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{Ar}-H), 3.89$ (brs, $12 \mathrm{H}, \mathrm{ArOCH}_{2}$ ), 1.21-1.39 (m, 108H, $\mathrm{CH}_{2}$ ), $0.79\left(\mathrm{t}, J=6.8 \mathrm{~Hz}, 18 \mathrm{H}, \mathrm{CH}_{3}\right.$ ). MALDI-TOF MS for $\mathrm{C}_{132} \mathrm{H}_{186} \mathrm{~N}_{6} \mathrm{O}_{12}$ (cacld. 2048.92): $m / z=2049.08\left([M]^{+}, 100 \%\right)$. UV/Vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \lambda_{\text {max }}(\mathrm{nm})\left(\varepsilon / \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right) 297(5.21 \times$ $\left.10^{4}\right), 379\left(1.12 \times 10^{5}\right)$. IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 2923\left(v_{\mathrm{CH} 2}\right), 2852\left(v_{\mathrm{CH} 2}\right), 1614\left(v_{\mathrm{HC}=\mathrm{N}}\right), 1514,1296$, 1186, 1115. Anal. Calcd. for $\mathrm{C}_{132} \mathrm{H}_{186} \mathrm{~N}_{6} \mathrm{O}_{12}$ : C, 77.38; H, 9.15; N, 4.10. Found: C, 77.11; H, 9.32; N, 4.16\%.
$\mathbf{T S Z n}_{3}$ : To a suspension of $\mathbf{T S H}_{6}(0.053 \mathrm{~g}, 0.026 \mathrm{mmol})$ in $\mathrm{MeOH}(20 \mathrm{~mL})$ was added a MeOH solution $(2 \mathrm{~mL})$ of $\mathrm{Zn}(\mathrm{II})$ acetate dihydrate $(0.034 \mathrm{~g}, 0.156 \mathrm{mmol})$, and the mixture was stirred at r.t. for 3 days. The precipitate was collected by filtration, washed with $\mathrm{MeOH}(10 \times 3$ mL ), and dried under vacuum, to give $\mathbf{T S Z n}_{3}(0.049 \mathrm{~g}, 0.022 \mathrm{mmol})$ as red orange solid in $86 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2} /\right.$ pyridine- $d_{5}, 95: 5$ in vol): $\delta(\mathrm{ppm}) 8.66$ (brs, $\left.6 \mathrm{H}, \mathrm{N}=\mathrm{CH}\right), 8.28$ (brs, 6 H , arene- H ), 7.19 (brs, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ ), 6.24-6.37 (m, $12 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ ), 3.95 (brs, $12 \mathrm{H}, \mathrm{ArOCH}_{2}$ ), 1.32-1.79 (m, 108H, $\mathrm{CH}_{2}$ ), 0.91 (brs, $18 \mathrm{H}, \mathrm{CH}_{3}$ ). MALDI-TOF MS for $\mathrm{C}_{132} \mathrm{H}_{180} \mathrm{Zn}_{3} \mathrm{~N}_{6} \mathrm{O}_{12}$ (cacld. 2239.04): $m / z=2238.46\left([M]^{+}, 100 \%\right)$. UV/Vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \lambda_{\text {max }}(\mathrm{nm})\left(\varepsilon / \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right) 334(6.78 \times$ $\left.10^{4}\right), 419\left(9.95 \times 10^{4}\right), 488\left(4.95 \times 10^{4}\right)$. IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 2924\left(v_{\text {СН2 }}\right), 2852\left(v_{\text {СН2 }}\right), 1611$ $\left(v_{\text {HC=N }}\right), 1585,1521,1435$. Anal. Calcd. for $\mathrm{C}_{132} \mathrm{H}_{180} \mathrm{Zn}_{3} \mathrm{~N}_{6} \mathrm{O}_{12} \cdot 6 \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 67.55 ; \mathrm{H}, 8.25 ; \mathrm{N}, 3.58$. Found: C, 67.19; H, 8.00; N, 3.66\%.
(3) Synthesis of Non-Alkyl-Tethered Zn(II) Trigon


Nonalkoxylated TSH: To a suspension of $\mathbf{4}(52.3 \mathrm{mg}, 0.097 \mathrm{mmol})$ in EtOH ( 3.0 mL ) was added $\mathrm{Et}_{3} \mathrm{~N}(89 \mathrm{mg}, 0.88 \mathrm{mmol})$ at r.t. under Ar. The mixture was stirred for 10 min , added with an EtOH ( 2.0 mL ) solution of 2-hydroxybenzaldehyde ( $0.107 \mathrm{~g}, 0.88 \mathrm{mmol}$ ), and the mixture was stirred at reflux temperature for 12 h . The suspension was cooled at $-10^{\circ} \mathrm{C}$ and stirred for another 1 h . The precipitate was collected by filtration, washed with cold EtOH, and dried under vacuum, to give a Nonalkoxylated TSH $_{6}(0.041 \mathrm{~g}, 0.044 \mathrm{mmol})$ as orange solid in $45 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta(\mathrm{ppm}) 12.91$ (brs, $\left.6 \mathrm{H}, \mathrm{OH}\right), 8.10(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}=\mathrm{N}) 7.39(\mathrm{~s}, 6 \mathrm{H}$, triphenylene CH ), $7.13(\mathrm{t}, J=7.2 \mathrm{~Hz}, 6 \mathrm{H}$, aromatic CH$), 7.01(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 6 \mathrm{H}$, aromatic $\mathrm{CH}), 6.72(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 6 \mathrm{H}$, aromatic CH$), 6.64(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}$, aromatic CH ). MALDI-TOF MS for $\mathrm{C}_{60} \mathrm{H}_{42} \mathrm{~N}_{6} \mathrm{O}_{6}$ (Cacld. 942.32), $m / z=942.87$ ([M] $\left.{ }^{+}, 100 \%\right)$. Anal. Calcd. for $\mathrm{C}_{60} \mathrm{H}_{42} \mathrm{~N}_{6} \mathrm{O}_{6}$ : C, 76.42; H, 4.49; N, 8.91. Found: C, 77.01; H, 4.30; N, 8.69\%.

Nonalkoxylated TSZn $\mathbf{3}_{3}$ : To a suspension of Nonalkoxylated TSH $_{6}$ ( $12.8 \mathrm{mg}, 0.014 \mathrm{mmol}$ ) in $\mathrm{MeOH}(6.0 \mathrm{~mL})$ was added a MeOH solution $(1.0 \mathrm{~mL})$ of $\mathrm{Zn}(\mathrm{II})$ acetate dihydrate $(0.018 \mathrm{~g}$, 0.08 mmol ), and the mixture was stirred at r.t. for 3 days. A red-orange precipitate was collected by filtration, washed with $\mathrm{MeOH}(5.0 \times 3 \mathrm{~mL})$, and dried under vacuum, to give a Nonalkoxylated TSZn $_{3}(0.0148 \mathrm{~g}, 0.013 \mathrm{mmol})$ as red-orange solid in $93 \%$ yield. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}$ ) $\delta(\mathrm{ppm}) 9.50(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}=\mathrm{N}), 9.25(\mathrm{~S}, 6 \mathrm{H}$, triphenylene CH$), 7.64(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, 6 H , aromatic CH$), 7.31(\mathrm{t}, J=7.2 \mathrm{~Hz}, 6 \mathrm{H}$, aromatic CH$), 6.79(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 6 \mathrm{H}$, aromatic CH ), 6.66 ( $\mathrm{t}, J=7.2 \mathrm{~Hz}, 6 \mathrm{H}$, aromatic CH ). MALDI-TOF MS for $\mathrm{C}_{60} \mathrm{H}_{36} \mathrm{~N}_{6} \mathrm{O}_{6} \mathrm{Zn}_{3}$ (Cacld. 1132.05), $m / z=1131.25\left([M]^{+}, 100 \%\right)$. Anal. Calcd. for $\mathrm{C}_{60} \mathrm{H}_{36} \mathrm{Zn}_{3} \mathrm{~N}_{6} \mathrm{O}_{6} \cdot 6 \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 58.06 ; \mathrm{H}$, 3.90; N, 6.77. Found: C, 58.19; H, 3.92; N, 6.44\%.
(4) Synthesis of Control Compounds $\mathbf{S H}_{\mathbf{2}}$ and $\mathbf{S Z n}$

$\mathbf{S H}_{2}$ : To a hot EtOH ( 1.0 mL ) solution of $o$-phenylenediamine $(110.8 \mathrm{mg}, 1.03 \mathrm{mmol})$ was added dropwise an $\mathrm{EtOH}(5.0 \mathrm{~mL})$ solution of 4-dodecyloxy-2-hydroxylbenzaldehyde ( 691 mg , 2.25 mmol ), and the mixture was stirred at reflux for 12 h . The mixture was cooled at $-10{ }^{\circ} \mathrm{C}$, and the resulted yellow precipitate was filtered, washed with cold EtOH , and dried under vacuum, to give $\mathbf{S H}_{2}(0.525 \mathrm{~g}, 0.77 \mathrm{mmol})$ as bright yellow solid in $75 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}) 13.58(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OH}), 8.53(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}=\mathrm{N}), 7.30-7.25(\mathrm{~m}, 4 \mathrm{H}$, aromatic CH$)$, $7.23-7.20(\mathrm{~m}, 2 \mathrm{H}$, core aromatic CH$), 6.52(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}$, aromatic CH$), 6.46(\mathrm{dd}, J=8.8$, $2.0 \mathrm{~Hz}, 2 \mathrm{H}$, aromatic CH ), $3.98\left(\mathrm{t}, J=6.4 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right.$ ), $1.78\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{2}\right), 1.27-1.44$ (m, 36H, alkyl CH), $0.88\left(\mathrm{t}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{CH}_{3}\right.$ ). MALDI-TOF MS for $\mathrm{C}_{44} \mathrm{H}_{64} \mathrm{~N}_{2} \mathrm{O}_{4}$ (Cacld. $684.49), m / z=685.32\left([\mathrm{M}+\mathrm{H}]^{+}, 100 \%\right)$. UV/Vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \lambda_{\max }(\mathrm{nm})\left(\varepsilon / \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right) 295(2.47 \times$ $\left.10^{4}\right), 331\left(3.06 \times 10^{4}\right)$. IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 2922\left(v_{\mathrm{CH} 2}\right), 2852\left(v_{\mathrm{CH} 2}\right), 1610\left(v_{\mathrm{HC}=\mathrm{N}}\right), 1583,1516$, 1472. Anal. Calcd. for $\mathrm{C}_{44} \mathrm{H}_{64} \mathrm{~N}_{2} \mathrm{O}_{4}$ : C, 77.15; H, 9.42; N, 4.09. Found: C, 76.88; H, 9.43; N, 3.96\%.

SZn: To the suspension of $\mathbf{S H}_{\mathbf{2}}(69.8 \mathrm{mg}, 0.101 \mathrm{mmol})$ in $\mathrm{MeOH}(10.0 \mathrm{~mL})$ was added a MeOH solution $(1.0 \mathrm{~mL})$ of $\mathrm{Zn}(\mathrm{II})$ acetate dihydrate $(0.044 \mathrm{~g}, 0.202 \mathrm{mmol})$, and the mixture was stirred at r.t. for 3 days. A bright yellow precipitate was collected by filtration, washed with $\mathrm{MeOH}(5.0 \times 3 \mathrm{~mL})$, and dried under vacuum, to give $\mathbf{S Z n}(0.065 \mathrm{~g}, 0.087 \mathrm{mmol})$ as bright yellow solid in $86 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta(\mathrm{ppm}) 8.32(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}=\mathrm{N}), 7.32-7.29(\mathrm{~m}$, 2 H , aromatic CH$), 7.25-7.22(\mathrm{~m}, 2 \mathrm{H}$, aromatic CH$), 6.90(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}$, aromatic CH$)$, $6.11(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 4 \mathrm{H}$, aromatic CH$), 3.80\left(\mathrm{t}, J=6.4 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right), 1.72\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{2}\right)$, 1.42-1.28 (m, 36H, alkyl CH ), $0.87\left(\mathrm{t}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{CH}_{3}\right)$. MALDI-TOF MS for $\mathrm{C}_{44} \mathrm{H}_{62} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Zn}$ (Cacld. 746.40), $m / z=747.47\left([\mathrm{M}+\mathrm{H}]^{+}, 60 \%\right), 769.47\left([\mathrm{M}+\mathrm{Na}]^{+}, 100 \%\right)$. UV/Vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \lambda_{\text {max }}(\mathrm{nm})\left(\varepsilon / \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right) 261\left(1.98 \times 10^{4}\right), 313\left(2.78 \times 10^{4}\right), 375\left(2.50 \times 10^{4}\right)$. IR (KBr): $v\left(\mathrm{~cm}^{-1}\right) 2921\left(v_{\mathrm{CH} 2}\right), 2851\left(v_{\mathrm{CH} 2}\right), 1612\left(v_{\mathrm{HC}=\mathrm{N}}\right), 1584,1527,1467,1432$. Anal. Calcd. for $\mathrm{C}_{44} \mathrm{H}_{62} \mathrm{ZnN}_{2} \mathrm{O}_{4} \cdot \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 68.96 ; \mathrm{H}, 8.42$; N, 3.66. Found: C, 68.88; H, 8.35; N, 3.59\%.

## Section 3. MALDI-TOF MS Spectral Profiles



Figure $\boldsymbol{S 1}$. MALDI-TOF MS spectral profiles of a) $\mathbf{T S H}_{6}$, b) $\mathbf{T S Z n}_{3}$, c) $\mathbf{S H}_{2}$ and d) $\mathbf{S Z n}$.

## Section 4. Absorption Coefficient Measurements



Figure $\boldsymbol{S 2}$. Plot of absorbance of $\mathbf{T S Z n}_{3}$ at 419 nm vs concentration in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. No aggregation was observed in this concentration region.

## Section 5. Gelation Experiment

Typical procedure: $\mathbf{T S Z n}_{3}(10 \mathrm{mg}, 4.48 \mu \mathrm{~mol})$ was added to decalin $(1 \mathrm{~mL})$ in a vial or quartz cell. Upon heating at $80^{\circ} \mathrm{C}, \mathbf{T S Z n}_{3}$ was dissolved to give a clear solution, which was allowed to stand at r.t. for 2 h . The formation of the gels was evaluated by the "stable to inversion of a test tube" method.

The gel-to-sol transition temperature was measured by the drop ball method. ${ }^{[9]]}$

Table $\boldsymbol{S 1}$. Gelation test of $\mathbf{T S H}_{6}$ and $\mathbf{T S Z n}_{3}$ in organic solvents ( $10 \mathrm{mg} / \mathrm{mL}$ ).

| Organic Solvents | State |  |
| :--- | :---: | :---: |
|  | TSH $_{6}$ | TSZn $_{3}$ |
| Benzene | S | S |
| Toluene | S | S |
| THF | S | S |
| Chloroform | S | S |
| Dichoromethane | S | S |
| Hexane | S | PG |
| Dodecane | S | PG |
| Cyclohexane | S | G (opaque) |
| Decalin | S | G (transparent) |
| Acetone | I | S |
| Diethylether | I | I |
| Methanol | I | I |

S: soluble, I: insoluble, G: gel, PG: partial gel.

## Section 6. Thermally Driven Sol-Gel Transition



Figure $\boldsymbol{S 3}$. Photos of the $\mathbf{T S Z n}_{3}$ gel in decalin $(4.5 \mathrm{mM})$ upon heating from 25 to $70^{\circ} \mathrm{C}$.


Figure $\boldsymbol{S 4}$. Photos of the $\mathbf{T S Z n}_{3}$ gel in decalin ( 9.0 mM ) upon heating from 25 to $60^{\circ} \mathrm{C}$. It showed that the steel ball laid on the top of the gel at $30^{\circ} \mathrm{C}$, dropped to the gel between 47-49 ${ }^{\circ} \mathrm{C}$, and finally sank to the bottom at $55^{\circ} \mathrm{C}$. The temperature for gel-to-sol transition was estimated to be $48{ }^{\circ} \mathrm{C}$.

## Section 7. Simulation and Calculation of Sheet Structure

The experimental PXRD pattern shows three different kinds of peaks corresponding to characteristic interatomic or interlayer distances resulted from the specific molecular arrangement of $\mathbf{T S Z n}_{3}$ (Figure $S 5$ ). The first sharp peak at $0.189 \AA^{-1}$ corresponds to the $d$-spacing of $33.19 \AA$, which is well matched with the interlayer distance between aliphatic chain along $b$-direction. Two broad peaks at $0.557 \AA^{-1}$ and $1.394 \AA^{-1}$ are comprised of several peaks, as shown in Fig. $S 6$. However, their calculated $d$-spacing values of $11.28 \AA$ and $4.51 \AA$ are also well matched with interatomic distance between $\mathrm{Zn}--\mathrm{Zn}$ in single $\mathbf{T S Z n}_{\mathbf{3}}$ molecule and interlayer distance between molecular plane along $c$-direction respectively.

Figure $S 7$ shows this molecular arrangement viewed along in $c$ - (up) and $b$-direction (down) in the P32 lattice. Simulated PXRD pattern (blue curve) is calculated from P32 unit cell and shows a good agreement with the experimental PXRD pattern (red curve). All molecular modeling and simulation of PXRD pattern were carried out using Reflex, a software package for crystal structure determination from PXRD pattern, implemented in MS modeling ver. 4.3 (Accelrys Inc.).


Figure S5. Experimental PXRD pattern and molecular arrangement. Three peaks in PXRD pattern show characteristic distances related to molecular arrangement of $\mathbf{T S Z n}_{3}$.


Figure S6. Comparison of simulated PXRD pattern (black and blue curves) from the P32 lattice with experimental one (red curve).


Figure $\boldsymbol{S 7}$. Construction of $P 32$ lattice with optimized $\mathbf{T S Z n}_{3}$ molecule in view along the $c$-direction (up) and along the $b$-direction (down). When the unit cell is elongated in $c$-direction, all atomic coordinates are exactly superposed at their positions.

## Section 8. Electric Conductivity of Control Samples



Figure S8. $I-V$ profiles of a) the $\mathbf{T S Z n}_{3}$ solid sample before assembly and b) the $\mathbf{S Z n}$ solid sample (black curve: the gap itself; red curve: the sample; blue curve: the sample doped with iodine).

## Section 9. Spectral Change Profiles of $\mathrm{TSZn}_{3}$ Sheet upon Doping with Iodine



Figure $\boldsymbol{S 9}$. a) Time-dependent FT IR spectral change of the $\mathbf{T S Z n}_{3}$ sheet upon doping with iodine (a typical new band appeared at $1023 \mathrm{~cm}^{-1}$ upon doping). b) Time-dependent electronic absorption spectral change of the $\mathbf{T S Z n}_{3}$ sheet upon doping with iodine (the absorption band blue-shifted from 428 to 382 nm ).

## Section 10. Cyclic Voltammetric Profile of $\mathrm{TSZn}_{3}$



Figure $\boldsymbol{S 1 0}$. Cyclic voltammetric profile of $\mathbf{T S Z n}_{3}$ in dichloromethane solution ( 0.5 mM ) containing $0.1 \mathrm{M} \mathrm{TBAPF}_{6}$. Potentials are reported versus the $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couple as an internal standard.

## Section 11. Photoconductivity of $\mathbf{T S Z n}_{3}$ Sheet on $\mathbf{1 0 - \mu}$ m-wide Pt Gap Electrodes



Figure $\boldsymbol{S 1 1}$. Photocurrent of the $\mathbf{T S Z n}_{3}$ Sheet on $10-\mu$ m-wide Pt Gap Electrodes when light is turned on or off.

## Section 12. Time-of-Flight Transient Current Integration



Figure $\boldsymbol{S 1 2}$. Time-of-flight transient current profile. The excitation was carried out by $355-\mathrm{nm}$ laser at $1.7 \times 10^{16}$ photons $/ \mathrm{cm}^{2}$. The current was obtained under 8 V bias voltage applied between $5 \mu \mathrm{~m}$ interdigitated electrodes.


Figure $\boldsymbol{S 1 3}$. Number of charge carriers for various bias voltages.

## Section 13. Supporting References

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