Supporting Information for:

Effect of Incorporating Flat Aromatic Molecules on Spherical Polymeric Nanoparticles

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Instruments

¹H and ¹³C NMR spectra were recorded by 400 MHz Bruker NMR spectrometer. Deuterated solvents peaks were used as internal standard peak. Atomic force microscopy (AFM) images were collected using a digital instrument dimension 3100 atomic force microscope operating in tapping mode. Transmission electron microscopy images were captured using JEOL JEM-2000FX operating at 200 KV. Dynamic light scattering (DLS) measurements were done by a Malvern Nanozetasizer and molecular weight of polymer was characterized by gel permeation chromatography (GPC).

Materials

All chemicals were purchased from commercial sources and used as received, unless otherwise mentioned. Tetrahydrofuran (THF) was distilled over sodium. Thiolactone acrylamide¹, *N*-Boc ethylenediamine and *N*-(2-Ethylhexyl) naphthalenetetracarboxylic monoanhydride monoimide² were synthesized as previous reports.

Synthesis of Thiolactone polyacrylamide (P1)



Mixture of thiolactone acrylamide (2.7 g, 16 mmol), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanoic acid (0.13 g, 0.325 mmol), and azobis(isobutyronitrile) (AIBN, 8 mg, 0.049 mmol) were dissolved in dried THF (15 mL). The solution was degased by four freeze-pump-thaw cycles. The reaction was sealed and placed into 60 °C pre-heated oil bath and stirred for 12 h. Then, the reaction was immediately quenched in liquid nitrogen. Additional THF was added and the polymer was precipitated in methanol. To further purification the polymer was reprecipitated in methanol three times and the precipitate was dried under vacuum to give light yellow powder (80% yield). GPC (THF) Mw 3,500 g/mol with polydispersity index of 1.12. ¹H NMR (DMSO): δ 4.86-4.31, 3.50-3.11, 2.60-2.34, 2.31-1.90, 1.69-1.15

Synthesis of the amphiphilic homopolymer (P3)



Thiolactone polyacrylamide (1 g) and aldrithiol (11.3 g, 58 mmol) were dissolved in dimethyl formamide (DMF). Solution of *N*-boc ethylenediamine (5.0 g, 29 mmol) in DMF was adding dropwise to the reaction over 45 mins (the solution color turns to yellow). The reaction was stirred at room temperature overnight. Then, the product was precipitated in diethyl ether. The precipitated was washed with diethyl ether three times to yield light yellow powder. The product was used to the next step without further characterizations. The polymer was dissolved in chloroform. 10 mL of trifluoroacetic acid (TFA) was added. The reaction was stirred at room temperature for 6 h. Then, the solution was concentrated and diethyl ether (100 mL) was added to the solution to precipitate the product. The solid was separated out and washed with diethyl ether 3 times to give light yellow powder. GPC (DMF) Mn 4,600 g/mol with polydispersity index of 1.15. (78% Yield) NMR (DMSO): δ 8.60-8.37, 8.30-7.65, 7.34-7.12, 4.48-4.00, 4.02-3.47, 3.46-3.09, 2.99-2.61, 2.23-1.80, 1.22-0.45.

Preparation of amine-based nanoparticles

1.5 mg/mL of 1 in deionized (DI) water was prepared to give the size of polymer nanoassembly of 50 nm. DL-dithiothreitol (0.5 equivalence) was added to the reaction. It was stirred at room temperature overnight. By products were removed by dialysis tubing (molecular weight cut off of \sim 3,500 Mw) in DI water for 2 days. The solvent was removed by lyophilizer to give white powder of the nanoparticle.

Synthesis of NDI-al



N-(2-Ethylhexyl) naphthalenetetracarboxylic monoanhydride monoimide (600 mg, 1.59 mmol) and 3-amino-1-propanol (140 mg, 1.75 mmol) was dissolved in DMF (10mL). The solution was refluxed for 12h. Water was then added to the reaction. The solid was collected by filtration and wash with water three times. The crude was dried under vacuum. The product was further purified by flash column chromatography (Dichloromethane/Methanol) to get pink solid (400 mg, 60%) ¹H NMR (CDCl₃): δ 8.77 (d, 4H), 4.38 (t, 2H), 4.15 (m, 2H), 3.64 (q, 2H), 2.62 (t, 1H), 2.02 (m, 2H), 1.94 (m, 1H), 1.25-1.45 (m, 8H), 0.94 (t, 3H), 0.88 (t, 3H).

The previous product (200 mg, 0.46 mmol) was dissolved in THF. The solution was cooled downed to 0 $^{\circ}$ C and methane sulfonylchloride (0.17 mL, 2.30 mmol) was added to the solution. The solution was warm up to room temperature and stirred for 3h. The solvent and excess reagents were removed under vacuum. The crude was dissolved in THF and lithium bromide was added in portions to the reaction. It was refluxed for another 10h. Solvents was removed and the crude product was purified by flash column chromatography (Dichloromethane /Methanol) to yield the light yellow solid (150 mg, 65%) ¹H NMR (CDCl₃): δ 8.77 (d, 4H), 4.37 (t, 2H), 4.15 (m, 2H), 3.51 (t, 2H), 2.36 (t, 2H), 1.94 (m, 1H), 1.25-1.45 (m, 8H), 0.94 (t, 3H), 0.88 (t, 3H). ¹³C NMR (CDCl₃): δ 163.1, 163.0, 131.1, 131.0, 126.8, 126.3, 44.6, 39.8, 37.9, 31.1, 30.7, 30.2, 28.6, 24.0, 23.0, 14.1, 10.6 El/Mass: Calc. 498.1154 found 498.1130

Synthesis of NDI-am



1, 4, 5, 8-napthalenetetracarboxylic dianhydride (400 mg, 1.49 mmol) and glycine (168 mg, 2.24 mmol) were dissolved in DMF. The reaction was heat to 140 $^{\circ}$ C and stirred for 10h. 2-ethyl-1-hexylamine (0.25 mL) was added to the reaction and it was stirred for further 6h. The reaction was then cooled down to room temperature. Water was added to the solution and the product was extracted by dichloromethane. The organic phase was dried over Na₂SO₄. The product was further purified by flash column chromatography (Dichloromethane/Methanol) to yield yellow solid (138 mg, 21%) ¹H NMR (CDCl₃): δ 8.78 (d, 4H), 5.02 (s, 2H), 4.15 (m, 2H), 1.94 (m, 1H), 1.25-1.45 (m, 8H), 0.94 (t, 3H), 0.88 (t, 3H), ESI/Mass: Calc. 436.1634 found 436.1626

Synthesis of NDI-am-C4



N-(2-Ethylhexyl) naphthalenetetracarboxylic monoanhydride monoimide (600 mg, 1.59 mmol) and Υ -amino butyric acid (180 mg, 1.75 mmol) were dissolved in DMF (10mL). The solution was refluxed for 12h. Water was then added to the reaction. The solid was collected by filtration and wash with water three times. The crude was dried under vacuum. The product was further purified by flash column chromatography (Dichloromethane/Methanol) to get white-pink solid (464 mg, 63%) ¹H NMR (CDCl₃): δ 8.76 (d, 4H), 4.29 (t, 2H), 4.14 (m, 2H), 2.50 (t, 2H), 2.11 (m, 2H), 1.94 (m, 1H), 1.25-1.45 (m, 8H), 0.93 (t, 3H), 0.88 (t, 3H). ¹³C NMR (CDCl₃): δ 176.9, 163.2, 163.0, 131.1, 131.0, 126.7, 126.4, 44.6, 39.9, 37.9, 31.2, 30.7, 28.6, 24.0, 23.1, 23.0, 14.1, 10.6 ESI/Mass: Calc. 464.1947 found 464.1932

Synthesis of NDI-am-C6



N-(2-Ethylhexyl) naphthalenetetracarboxylic monoanhydride monoimide (165 mg, 0.44 mmol) and \mathcal{E} -amino caproic acid (86 mg, 0.656 mmol) were dissolved in DMF (5 mL). The solution was refluxed for 12h. Water was then added to the reaction. The solid was collected by filtration and wash with water three times. The crude was dried under vacuum. The product was further purified by flash column chromatography (Dichloromethane/Methanol) to get white-pink solid (151 mg, 70%) ¹H NMR (CDCl₃): δ 8.78 (s, 4H), 4.20 (t, 2H), 4.14 (m, 2H), 2.39 (t, 2H), 1.94 (m, 1H), 1.74 (m, 4 H), 1.50 (m, 2 H)1.25-1.45 (m, 8 H), 0.93 (t, 3H), 0.88 (t, 3H). ¹³C NMR (CDCl₃): δ 178.5, 163.2, 162.8, 131.0, 126.7, 126.6, 126.5, 44.6, 40.6, 37.9, 33.6, 30.7, 28.6, 27.7, 26.4, 24.3, 24.0, 23.0, 14.1, 10.6 El/Mass: Calc. 492.2260 found 492.2236

Synthesis of NDI-acid chloride derivatives

For all NDI-am, NDI-am-C4, and NDI-am-C6, the carboxylic acid group was converted to highly reactive acid chloride to future functionalize onto amine-based nanoparticle. NDI was dissolved in chloroform and 5x mole excess of thionyl chloride was added. The reaction was refluxed 6h. The excess reagent and solvent was removed under vacuum to give NDI-acid chloride derivatives in quantitative yield.

Pyrene functionalized spherical nanoparticle

Pyrene-1-carboxylic acid was converted into acid chloride derivative and functionalized onto the nanoparticle using the same procedure. Pyrene was functionalized onto the nanoparticle to understand molecular alignment on the particle surface, since the pyrene is capable of forming excimer when packed close together. Thin films were prepared by spin coating solution in chloroform on transparent glass at 1,000 RPM for 60s. The results show that the solid film exhibited strong excimer signal, with negligible amount of monomeric emission. On the other hand, the partially functionalized pyrene nanoparticle exhibits both monomer and excimer signals. This supports our hypothesis that high density packing would be observed, when the nanoparticle surface is fully functionalized.



Fig. S1. Light emission under 350 nm illumination (left) and emission spectra (right) of pyrenefunctionalized NP





P1 polymer























Synthesis of NDI-functionalized nanoparticle

Amine-based nanoparticle was dispersed in chloroform (2 mg/mL). The solution was vigorously stirred and put in ultra sonicator for 30 mins. Then, 10x mole excess of NDI (acid chloride derivatives or NDI-al) compared to amine functional groups was added to the dispersion. The reaction was stirred at room temperature for 10 h and triethyl amine was added to neutralize the dispersion. The excess reagent was removed by dialysis tubing (molecular weight cut off of ~3,500 Mw) in dichloromethane for 2 days. The solvent was evaporated to yield powder-like solid.



Fig. S2. Size distribution of amine-based nanoparticle (in water, green), NP-al (in chloroform, blue), and NP-am (in chloroform, red)

OFET fabrication

The pre-patterned n-doped silicon substrate organic field effect transistor (OFET) devices were purchased from Fraunhofer Institute for photonic microsystem IPMS. The OFET architecture was bottom contact gold electrode. The channel width of all transistors was 10 mm. The channel length was 2.5, 5, 10 or 20 μ m. The capacitance of the insulator is 14.9 nF cm⁻² for 230 nm of SiO₂. The protective layer on OFET devices was removed by washed with acetone three times and the device was dried under inert atmosphere. Organic thin films were deposited on the surface by spin coating of 1 mg mL⁻¹ chloroform solution at 1000 RPM for 60 s and then they were dried at room temperature in a glove box. All devices were analyzed by using an Agilent 4165C precision semiconductor parameter analyzer under inert atmosphere at room temperature.

Table 1. Field effect charge carrier mobilities μe ĥe Vthreshold Ion/off (cm² V⁻¹ (cm²V⁻¹ s⁻¹ S 10^{4} NDI-amC4 $2.41 \pm 2.36 \times 10^{-1}$ 6.45 x 10⁻ 24 V 1.38 ± 1.07 x 10⁻⁵ 2.66 x 10⁻⁵ 10⁴ NP-amC4 60 V 8.88 ± 9.14 x 10⁻⁶ 2.39 x 10⁻⁵ 10⁴ NDI-amC6 36 V <u>10</u>⁴ 4.08 ± 3.56 x 10⁻⁵ 8.75 x 10⁻⁵ NP-amC6 77 V





Fig. S3. Output (left) and transfer (right) characteristics of OFET devices of a) NDI-al, b) NP-al, c) NDI-am, d) NP-am, e) NDI-amC4, f) NP-amC4, g) NDI-amC6, and h) NP-amC6

Gold is used as both source and drain electrodes in all prefabricated FET devices in this study, since gold has the capability to inject both hole and electron. The reason for the lack of saturation regime in the current-voltage (drain) curves is attributed to the Schottky barrier at the gold / semiconductor interface.

SCLC fabrication

ITO coated glass were washed in acetone, ethanol and isopropanol in an ultrasonic bath respectively. ITO surface was treated with UV-ozone for 15 min. A zinc acetate precursor solution which prepared from the solution of zinc acetate dihydrate (196 mg) and ethanolamine (54 μ L) in ethanol (stirred for 2 hr at 45°C before use) was spin cast onto the cleaned substrates at 4,000 rpm for 60 s. The devices were then heated on a hot plate at 180°C for 60 min. The coated substrates were used for spin-coating active layer in glove box with a controlled atmosphere (O₂, H₂O < 0.1ppm) as following procedure: 1 mg mL⁻¹ solution in chloroform was coated on the substrates at at 1000 RPM for 60 s and solvent was allowed to evaporate at room temperature in the glove box (100-150 nm of active layer thickness). The substrates were transferred to thermal evaporator. A 70 nm thick calcium layer was deposited onto the substrate

at rate of 0.1 nm s⁻¹ under vacuum (10^{-6} bar). The devices were characterized by Keithley 2600 series multimeter.

Charge mobility of all materials was calculated using modified Mott-Gurney equation where mobility is independent from field:

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 e^{\beta \sqrt{E}} \frac{E^2}{d}$$

J is current density, ε is relative permittivity (~3 for organic compound), ε_0 is absolute permittivity, μ_0 is zero field mobility, β is Poole-Frenkel factor, E is electric field, and d is sample thickness.



Fig. S4. Graph between In (Jsc/E²) and E^{1/2} of NDI-am, NDI-amC6, and NDI-al for both nanoparticle (NP) and small molecule (NDI) before (left) and after (right) annealing at 150 °C for 30 min.

Table 2 SCLC charge mobility		
	Before annealing	After annealing
NDI-am	6.6 ± 1.4 x 10 ⁻⁵ cm ² s ⁻¹ V ⁻¹	7.7 x 10 ⁻⁷ cm ² s ⁻¹ V ⁻¹
NP-am	1.7 ± 0.5 x 10 ⁻⁴ cm ² s ⁻¹ V ⁻¹	1.7 ± 0.4 x 10 ⁻⁴ cm ² s ⁻¹ V ⁻¹
NDI-amC6	8.6 ± 7.0 x 10 ⁻⁵ cm ² s ⁻¹ V ⁻¹	5.5 ± 5.0 x 10 ⁻⁵ cm ² s ⁻¹ V ⁻¹
NP-amC6	9.2 ± 1.5 x 10 ⁻⁵ cm ² s ⁻¹ V ⁻¹	1.9 ± 0.5 x 10 ⁻⁴ cm ² s ⁻¹ V ⁻¹
NDI-al	$1.2 \pm 0.1 \times 10^{-4} \text{ cm}^2 \text{s}^{-1} \text{ V}^{-1}$	3.3 ± 3.0 x 10 ⁻⁵ cm ² s ⁻¹ V ⁻¹
NP-al	1.0 ± 0.1 x 10 ⁻⁴ cm ² s ⁻¹ V ⁻¹	$1.4 \pm 0.3 \times 10^{-4} \text{cm}^2 \text{s}^{-1} \text{V}^{-1}$

Estimation of percent volume occupied by NDI on nanoparticle surface



NDI-functionalized nanoparticles exhibit charge conductivity event though the availability of NDI is very small compared to the insulator nanoparticle core. It is crucial to demonstrate how much NDI contains in this type of system. Here, we approximately calculate the percent occupied volume of NDI-al by the following:

The size of the functionalized nanoparticle is close to 90 nm in both NP-al and NP-am based on dynamic light scattering. Assuming that the nanoparticles have perfect spherical shape, thereby, the volume of the functionalized is roughly calculated to be 382,000 nm³. Then, the length of NDI-al from head to tail is estimated to be 1.8 nm by Molview 3d model. Assuming that 1.8 nm is the length that NDI-al occupying on the nanoparticle surface, then, the volume taken by NDI-al is calculated to be around 44,000 nm³ which is about 12% of the total volume of the functionalized nanoparticle. More than 88% by volume is occupies by the insulator nanoparticle core. Nonetheless the functionalized nanoparticle still holds charge transport characteristic close to the small molecule counterpart. This can be contributed to high surface functionalization of NDI on the nanoparticle. This logical estimation reveals the potential of utilizing polymeric nanoparticle as a scaffold for building a spherical nanostructure of charge transport material.



Fig. S5. AFM images of NDI-am (left) and NP-am (right) films after annealing at 150 $^{\rm o}{\rm C}$ for 30 min.

Thermal gravimetric analysis (TGA)

3 mg of the nanoparticle was placed in platinum pan. The sample was heated up to 600 °C in air at rate of 10 °C per minute. TGA thermogram was recorded. The observed 3% weight loss at the beginning before 100 °C was due to the moisture in the cross-linked polymer. The polymer

started degrading after 200 °C. This shows that the polymer is not decomposed at annealing temperature.



Fig. S6. TGA thermogram of amine-based nanoparticle

Differential scanning calorimetry (DSC)

2 mg of nanoparticle was placed into aluminum pan. The sample was equilibrated and heated at rate of 10 °C per minute. DSC thermograms were recorded. Since the nanoparticle was prepared from cross-linked polymer, phase transitions such as glass transition or polymer melting were not expected to be observed. The DSC thermogram also confirms that there is no phase transition detected between 20 °C to 160 °C.



Fig. S7. DSC thermogram of amine-based nanoparticle

Study of Nile red adsorption on cross-linked nanoparticle

1 mg of the nanoparticle was dispersed in 2 mL of chloroform. Nile red was added into the mixture in excess. It was stirred at 60 °C for 24 h. The mixture was cooled down to room temperature and was then transferred into dialysis tube (Molecular weight cut off of 3,500). It was dialysis against chloroform for 3 days. The absorption and emission spectra were recorded. The results showed that the dye molecule was almost completely removed after 2 days. The UV absorption was not able to detect the presence of Nile red and only small fluorescent signal was

observed. This supports our assertion that there is no encapsulated or adsorbed small molecules in the nanoparticle.



Fig. S8. Absorption (left) and emission (right) spectra of the mixture of amine-based nanoparticle and Nile red after dialysis for 1-3 days

References

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