Star-shaped nanographenes are large monodisperse polycyclic aromatic hydrocarbons that extend in size beyond the nanometer and have shown a lot of promise in a wide range of applications including electronics, energy conversion and sensing. Herein we report a new family of giant star-shaped N-doped nanographenes with diameters up to 6.5 nm. Furthermore, the high solubility of this SNG family in neutral organic solvents at room temperature allowed a complete structural, optoelectronic and electrochemical characterisation, which together with charge transport studies illustrate their n-type semiconducting character.
Giant Star-shaped Nitrogen-doped Nanographenes

Juan P. Mora-Fuentes,[a] Alberto Riaño-Carnerero,[a] Diego Cortizo-Lacalle,[a] Akinori Saeki,[b] Manuel Melle-Franco,*[c] Aurelio Mateo-Alonso*[a,d]

[a] POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, E-20018 Donostia-San Sebastian, Spain Fax: (+)34 943 50 6062 E-mail: amateo@polymat.eu
[b] Department of Applied Chemistry, Graduate School of Engineering, Osaka University Suita, Osaka 565-0871, Japan.
[c] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro 3810-193 Aveiro, Portugal
[d] Ikerbasque, Basque Foundation for Science E-48011 Bilbao, Spain

Abstract

Star-shaped nanographenes are large monodisperse polycyclic aromatic hydrocarbons that extend in size beyond the nanometer and have shown a lot of promise in a wide range of applications including electronics, energy conversion and sensing. Herein we report a new family of giant star-shaped N-doped nanographenes with diameters up to 6.5 nm. Furthermore, the high solubility of this SNG family in neutral organic solvents at room temperature allowed a complete structural, optoelectronic and electrochemical characterisation, which together with charge transport studies illustrate their n-type semiconducting character.
Nanographenes (NGs) are large monodisperse polycyclic aromatic hydrocarbons that extend in size beyond the nanometer and have shown a lot of promise in a wide range of applications including electronics, photonics, and energy. Atomically-precise control over the NG structure is crucial to fully exploit their potential. For instance, by controlling the number of rings, their arrangement, heteroatom-doping and substitution, it is possible to fine-tune their energy levels and therefore, modulate electron affinities, ionization potentials, energy gaps, absorption and emission properties, among others.

Among these, planar threefold symmetric star-shaped nanographenes (SNGs), such as starphenes, cloverphenes and their extended derivatives (Figure 1), have shown a prominent position as materials for charge transport, energy conversion and storage, light-emitting and sensing applications. However, even if, there have been very impressive advances in recent years and large SNGs diameters reaching 3.0 nm (55 condensed rings) have been reported by solution synthesis, the largest soluble SNG that has been fully characterised presents a diameter of 2.8 nm (16 condensed rings). This is because of the lack of solubility of planar π systems that extend in two dimensions, which tend to aggregate strongly by π-stacking in solution (Figure 1). In fact, the synthesis of extended SNGs is still a challenging task that requires dealing with insoluble intermediates and products, which overall makes synthesis, purification, characterisation and processing difficult, slowing down the exploration of their fundamental properties and the development of potential applications.
Figure 1. The SNG family (SNG-G\textsubscript{0}, SNG-G\textsubscript{1} and SNG-G\textsubscript{2}) described in this work, in comparison to representative SNGs synthesised by solution methods.
Herein we report a new family of giant SNGs that show diameters exceeding those of
the largest SNGs (3 nm) and that have been fully characterised thanks to their high
solubility (Figure 1). For instance, the first generation of this family (SNG-G₁) shows a
diameter of 4.1 nm (34 condensed rings), and remarkably, the second generation
(SNG-G₂) shows a diameter of 6.5 nm (55 condensed rings). As we show below, the
synthesis of this SNG family is not trivial and requires the careful design of a key C₃-
symmetrical precursor (SNG-G₀), from which the aromatic core can be then extended
radially. Furthermore, the high solubility of this SNG family in neutral organic solvents
at room temperature allowed a complete structural, optoelectronic and
electrochemical characterisation that together with charge transport studies illustrate
their n-type semiconducting character.

On a first approach, we aimed at synthesising SNGs by cyclocondensation of
precursor A⁴ to the commercially available cyclohexane-1,2,3,4,5,6-hexaone (HKT)
(Scheme 1a), which has been broadly used for the synthesis of
hexaazatriphenylenes and hexaazatrinaphthylenes.³ᵃ, ⁵ We selected precursor A,
which consists on a dibenzodiazatetracene core with terminal protected ketones in
the pyrene end and diamino groups at the quinoxaline end that enables an iterative
reaction scheme, as it can be assembled with itself by a set of
cyclocondensation/deprotection reactions. In addition, A possesses a combination of
tert-butyl and tri-iso-butylsilyl (TIBS) groups that have proven to render large NGs
soluble. However, when we carried out the cyclocondensation between building
block A and HKT in the solvent mixtures typically used for this type of
cyclocondensations, the reaction did not provide the expected cycloadduct B and
instead, yielded an inseparable mixture of compounds. We exposed this mixture of
compounds to Bunz oxidation conditions (MnO₂), which have proven to be useful to
aromatise mildly incomplete dihydro intermediates of azaacenes and their
derivatives,⁶ and the mixture evolved to a major compound. Structural
characterisation of such compound confirmed the formation of linear \( C_2 \) ribbon-like condensation adduct \( C \) with 13 fused aromatic rings (Scheme 1a). Therefore, we can safely attribute the formation of \( C \) to the early formation of a mixture of dihydro species of the dicondensation product that was fully aromatised afterwards by \( \text{MnO}_2 \), in line with several cases that have been noted in recent literature.\(^7\) The formation of the \( C_2 \) instead of the \( C_3 \) condensation was surprising since some of us reported the synthesis of the structurally equivalent hexa(TIBS)acetylene-substituted hexaazatrinaphthylene\(^8\) and the reaction proceeded without problems to the desired product. Nevertheless, the formation of the \( C_2 \) condensation product can be rationalised in terms of both nucleophilicity and steric hinderance because of the lower nucleophilicity of the diamines on the quinoxaline residue of \( A \) in comparison to phenylenediamine derivatives, which are unable to overcome the steric hinderance of the \( C_3 \) condensation product.
Scheme 1. a) Attempted synthesis of precursor B, leading to compound C instead.
b) Synthesis of SNG-G₀, SNG-G₁ and SNG-G₂.
At this stage, we changed strategy (Scheme 1b) and designed a new C₃ symmetrical precursor in which the three sets of diones are far apart from each other and at the same time are close to tert-butyl solubilizing groups that should not interfere sterically with the TIBS groups present at A during the triple cyclocondensation step. We therefore condensed pyrene diketone D[9] that can be obtained in 4 steps from pyrene and 1,2,3,4,5,6-hexaaminobenzene (HAB)[5] that can be obtained in 3 steps from 1,3,5-trichlorobenzene. The cyclocondensation proceeded without problems and yielded the hexaone-protected precursor SNG-G₀ in a good yield (45%). The deprotection of the terminal o-diones in the presence of TFA and water yielded the hexaone-terminated precursor SNG-G₀-Q (70%). The cyclocondensation reaction between A and SNG-G₀-Q proceeded without any problems and yielded SNG-G₁ after chromatographic purification (32%). The deprotection of the terminal diones in water/TFA, followed by cyclocondensation with A yielded the desired SNG-G₂ (38%).

The whole SNG series were remarkably soluble in toluene, and chlorinated solvents at room temperature and we were able to establish unambiguously their structure by ¹H-NMR and ¹³C-NMR spectroscopy and matrix-assisted laser desorption/ionization time of flight high-resolution mass spectrometry (MALDI-TOF HRMS). The ¹H-NMR and ¹³C-NMR spectra showed remarkably sharp signals that allowed confirming the structure in all the SNGs, illustrating the high solubility of the whole series. For instance, the integration of ¹H-NMR signals are in agreement with the structures of the SNGs (Figure 2a), integrating 6 protons for the aromatic signals a and b in SNG-G₀, SNG-G₁ and SNG-G₂, 6 protons for the aromatic signals e and f in the case of SNG-G₁ and SNG-G₂, 12 protons for the aromatic signal j in the case of SNG-G₂ (the assignments correspond to the lettering in Figure 1). While in SNG-G₀, SNG-G₁ and SNG-G₂, 12 protons for the terminal diketal signals c were observed in all cases, which is also consistent with the structure.[10] Further evidence of the successful preparation of the SNGs came from MALDI-TOF HRMS that show ion peak masses
(M+Ag)$^+$ of 1553.5692, 4211.1790, and 6868.7884 Da, respectively for SNG-G$_0$, SNG-G$_1$, and SNG-G$_2$, that matched with the expected mass. The isotopic distributions could be only recorded for SNG-G$_0$ and SNG-G$_1$ due to the high molecular weight of SNG-G$_2$, which is at the detection limit of the technique that illustrates the extremely high molecular weight of these monodisperse systems. Since we were not able to obtain single crystals suitable for X-ray diffraction, semiempirical quantum mechanics were used to investigate the structure of SNGs with the GFN-xTB method (Geometry, Frequency, Non-covalent, eXtended Tight-Binding) that allows computing efficiently high molecular weight systems with thousands of atoms.$^{[4, 11]}$ The simulations show that the SNG series can adopt a plethora of slightly twisted conformations as the result of the bulkiness and the TIBS groups (Figure S1), but that given the inherent flexibility of the iso-propyl substitutents the energies for interconversion between conformations is very small, which gives rise to nearly planar structures on average. The simulations show that the SNGs possess stable disk structures with diameters of 1.7, 4.1 and 6.5 nm respectively for SNG-G$_0$, SNG-G$_1$ and SNG-G$_2$. 
Figure 2. a) \(^1\)H-NMR spectra in CDCl\(_3\). The assignments correspond to the lettering in Figure 1. The stars indicate residual solvent peaks. b) UV-vis electronic absorption and c) photoluminescence spectra in CHCl\(_3\). d) Cyclic voltammograms in an Ar-saturated 0.1 M solution of nBu\(_4\)NPF\(_6\) in CH\(_2\)Cl\(_2\). Potentials versus Fc/Fc\(^+\). d) TRMC (\(\lambda = 355\) nm, \(I_0 = 9.1 \times 10^{15}\) photons/cm\(^2\)).
Thanks to the enhanced solubility, we could easily investigate the optoelectronic properties in solution. The absorption spectra of the SNGs were recorded in CHCl₃ and showed sets of absorption bands also consistent with their structure (Figure 2b). The electronic absorption spectrum of SNG-G₀ is dominated by 3 bands at 357, 402 and 428 nm, with a molar attenuation coefficient of (68,429 Lmol⁻¹cm⁻¹) for the longest wavelength transition (Figure 2b). The absorption bands of SNG-G₁ (354, 525 and 604 nm) and SNG-G₂ (373, 541 and 605 nm) appear bathochromically shifted in comparison with those of SNG-G₀ as consequence of the extension in the effective conjugation, which allows identifying three main absorption bands with their corresponding vibronic features. These were assigned as the α, ρ and β bands from longer to shorter wavelengths (Figure 2b), in agreement with previous assignments on pyrene-fused systems. The spectra showed that while the α band remains at almost invariable energies, the β and the ρ bands are increasingly shifted towards lower energies as a result of the radial extension of the π-system. Remarkably, also the molar absorptivity (ε) increases together with the diameter of the SNG, as exemplified by comparing the ρ bands of SNG-G₁ (448,985 Lmol⁻¹cm⁻¹) and SNG-G₂ (629,021 Lmol⁻¹cm⁻¹). The experimental electronic absorption spectra are in agreement with the calculated ones, which do not only corroborate the electronic structure but also shine light on the nature of the electronic transitions (Figure S2 and Table S1). In fact, time-dependent density functional theory (TD-DFT) and frontier orbital energies were computed with the 6-31g(d) basis set with the B3LYP Hamiltonian for SNG-G₀-H, SNG-G₁-H, and SNG-G₂-H, in which the TIBS groups on the acetylenes have been replaced by H atoms in order to reduce the calculation time due to the large size of the SNGs. A comparison of key electronic properties for both, GFN-xTB and B3LYP, Hamiltonians show that the differences due to this approximation are small and mostly negligible (Tables S2 and S3). The calculations show absorption spectra with the same trends as the experimental ones.
in terms of energies and intensities, in which the spectrum of SNG-G₀-H also differs from the spectra of SNG-G₁-H and SNG-G₂-H (Figure S2). The first lower energy band in SNG-G₁-H and SNG-G₂-H – consistent with the experimental α band – originates from transitions between the degenerate HOMOs and LUMOs (Figure S4). The second band – consistent with the experimental ρ band – originates from the transitions between a set of lower energy non-frontier degenerate HOMO orbitals (HOMO–3 and HOMO–4 for SNG-G₁-H, and HOMO–6 and HOMO–7 for SNG-G₂-H) to the degenerate LUMOs (Figure S5).

Remarkably, all three SNGs are emissive regardless of their size and their photoluminescence spectra are also consistent with their electronic structure. The emission spectrum of SNG-G₀ in CHCl₃ (λₑₓ = 340 nm) exhibited a band at 443 nm (quantum yield (Φ) = 0.26[13]). Meanwhile, the photoluminescence spectra of SNG-G₁ and SNG-G₂ (λₑₓ = 524 and 540 nm, respectively) in CHCl₃ show an isoenergetic emission band at 623 nm (Φ = 0.27 and 0.15,[14] respectively), since the emission originates in both cases from the α absorption band that is diameter independent. However, the emission of SNG-G₁ and SNG-G₂ is bathochromically shifted in comparison to SNG-G₀, as the result of the extended conjugation of the π-system.

The electrochemical properties of the SNGs were investigated by cyclic voltammetry in CH₂Cl₂ using nBu₄NPF₆ (0.1 M) as electrolyte and ferrocene/ferrocenium (Fc/Fc⁺) as internal standard (Figure 2d). The cyclic voltammograms show several reduction processes, while no oxidation processes were observed within the solvent-electrolyte window. From the cyclic voltammograms of SNG-G₀ four reduction waves could be identified at potentials more negative than –1.5 V, while only three reduction waves at more positive potentials (between –0.5 and –2.0 V) were identified for SNG-G₁ and SNG-G₂, in agreement with the extended conjugation of the π-system.
broader and more anodically shifted in the case of \textbf{SNG-G}_2, which is consistent with both the extended conjugation and multiple degenerate LUMO orbitals (Figures S3-S5).

The energy levels were estimated from the electronic spectra and the cyclic voltammograms. We estimated the energy gaps ($E_{\text{gap}}$) from the absorption onset of the longest absorption wavelength with values of 2.78, 1.98 and 1.97 eV for \textbf{SNG-G}_0, \textbf{SNG-G}_1 and \textbf{SNG-G}_2, respectively. These $E_{\text{gap}}$ values follow the same trends as the theoretical values (B3LYP-6-311+g(2d,g)/B3LYP-6-31g(d)) of \textbf{SNG-G}_0-H, \textbf{SNG-G}_1-H and \textbf{SNG-G}_2-H (Tables S2 and S3). The LUMO levels ($E_{\text{LUMO}}$) were estimated from the onset of the first reduction potential ($E_{\text{LUMO}} = -4.8 - e(E_{\text{ONSET}} - E_{1/2})$). The $E_{\text{LUMO}}$ of \textbf{SNG-G}_0, \textbf{SNG-G}_1 and \textbf{SNG-G}_2 were $-3.24$, $-3.98$ and $-4.00$ eV, respectively, which match reasonably well in absolute terms and very well in relative terms with the theoretical values (B3LYP-6-311+g(2d,g)/B3LYP-6-31g(d)) of \textbf{SNG-G}_0-H, \textbf{SNG-G}_1-H and \textbf{SNG-G}_2-H (Tables S2 and S3). The HOMO levels ($E_{\text{HOMO}}$) have been calculated from the difference between $E_{\text{LUMO}}$ and $E_g$ and were the following: $-6.02$, $-5.96$ and $-5.97$ eV for \textbf{SNG-G}_0, \textbf{SNG-G}_1 and \textbf{SNG-G}_2, respectively.

To assess the charge transporting properties of SNGs, we performed time-resolved microwave conductivity measurements (TRMC)\textsuperscript{[15]} directly on the solids powders (Figure 2e and Table S4). TRMC allows calculating the pseudo-photoconductivity values ($\phi \Sigma \mu_{\text{max}}$), which can be considered the intrinsic or minimum charge carrier mobility of the material, without the need of contacts. For instance the $\phi \Sigma \mu_{\text{max}}$ values correspond to the sum of the hole and electron mobilities ($\Sigma \mu$) times the quantum yield ($\phi$). We obtained nearly invariable $\phi \Sigma \mu_{\text{max}}$ values in the order of $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ with average $\phi \Sigma \mu_{\text{max}}$ values of 1.05 x $10^{-4}$, 0.98 x $10^{-4}$ and 1.11 x $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for \textbf{SNG-G}_0, \textbf{SNG-G}_1 and \textbf{SNG-G}_2, respectively, which are similar to those obtained for ribbon-like NGs,\textsuperscript{[4]} $\pi$-gels\textsuperscript{[16]} and conjugated polymers.\textsuperscript{[17]} Similarly, nearly invariable half lifetimes ($\tau_{1/2}$) of 0.45, 0.65 and 0.50 µs for \textbf{SNG-G}_0, \textbf{SNG-G}_1 and \textbf{SNG-G}_2.
respectively, were measured. The nearly invariable $\phi \Sigma \mu$ and $\tau_{1/2}$ values observed are consistent with observed localized states.

In this work, we have reported the synthesis of highly soluble SNGs with diameters up to 6.5 nm (55 condensed rings), which doubles those of the largest SNGs. Their synthesis has been achieved by a careful design and synthesis of a $C_3$-symmetrical precursor from which the SNG core is then extended radially. Most importantly, this approach provides highly soluble SNGs, which has allowed their synthesis and purification by solution methods and also a full characterisation (1H and 13C NMR, HRMS, UV-vis, photoluminescence, cyclic voltammetry and TRMC) that show how the radial extension of the π-system results in changes in their electronic absorption, molar absorptivity, photoluminescence and electrochemistry, while other properties remain almost invariable, such as the photoluminescence of the higher SNGs and the charge transport properties. The high molar absorptivity, low LUMO energies and $\phi \Sigma \mu$ values illustrate the $n$-type semiconducting character and their potential in charge transport and energy conversion applications.
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Giant Star-shaped Nitrogen-doped Nanographenes

Supporting Information

Juan P. Mora-Fuentes,[a] Alberto Riaño-Carnerero,[a] Diego Cortizo-Lacalle,[a] Akinori Saeki,[b] Manuel Melle-Franco,[c] Aurelio Mateo-Alonso*[a,d]

[a] POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, E-20018 Donostia-San Sebastian, Spain Fax: (+)34 943 50 6062 E-mail: amateo@polymat.eu

[b] Department of Applied Chemistry, Graduate School of Engineering, Osaka University Suita, Osaka 565-0871, Japan.

[c] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro 3810-193 Aveiro, Portugal

[d] Ikerbasque, Basque Foundation for Science E-48011 Bilbao, Spain
Figure S1. SNG-G_0 (left), SNG-G_1 (middle) and SNG-G_2 (right) computed with GFN-xTB.
Figure S2. Absorption spectra for SNG-G₀-H, SNG-G₁-H and SNG-G₂-H at the B3LYP-6-31g(d) level in vacuum (96 excitations), the simulated spectra (intensity vs. wavelength) is represented by a continuous line, while the oscillator strength of each transition is represented by sticks.
| Trans. | eV | nm  | Osc. Strength | Major contribs                        |
|--------|----|-----|---------------|---------------------------------------|
| SNG-G₀-H | 1  | 3.1 | 402           | 0.24 HOMO->LUMO (93%)                 |
| SNG-G₀-H | 11 | 3.4 | 364           | 0.95 H-1->L+1 (44%), HOMO->L+2 (44%) |
| SNG-G₁-H | 1  | 2.1 | 597           | 0.04 HOMO->LUMO (96%)                 |
| SNG-G₁-H | 10 | 2.4 | 519           | 1.32 H-3->L+1 (41%), H-4->LUMO (16%), H-4->L+1 (21%) |
| SNG-G₂-H | 1  | 2.0 | 613           | 0.01 HOMO->L+1 (96%)                  |
| SNG-G₂-H | 28 | 2.3 | 541           | 2.98 H-6->L+1 (27%), H-6->L+2 (26%), H-7->L+1 (18%) |

**Table S1.** TD-DFT first and strongest transitions at the B3LYP-6-31g(d) level for SNG-G₀-H, SNG-G₁-H, and SNG-G₂-H. All values in eV.
Figure S3. B3LYP-6-31g(d) level frontier orbitals for SNG-G0-H.
Figure S4. B3LYP-6-31g(d) level frontier orbitals for SNG-G₁-H.
Figure S5. B3LYP-6-31g(d) level frontier orbitals for SNG-G$_2$-H.
is geometries. The colour code is G0, 1, 2.

Optimisations were carried out using the GFN-xTB level. All values are in eV. Table S2. Frontier orbitals were computed with the B3LYP Hamiltonian with the 6-31g(d) basis set in vacuum for all geometries and the 6-311+g(2d,p) basis set for the SNG-Gx-H geometries. SNG-Gx molecules were optimised only at the GFN-xTB level while SNG-Gx-H geometries were optimised at the GFN-xTB and the B3LYP-6-31g(d) levels. The colour code is LUMOs, HOMOs and gaps. All values in eV.

| SNG-Gx | G0 | G1 | G2 |
|--------|----|----|----|
| -0.76  | -0.8 | -0.8 | -0.92 |
| -1.64  | -1.68 | -1.67 | -2.31 |
| -2.35  | -2.36 | -2.51 | -3.17 |

Table S3. Frontier orbitals eigenvalues B3LYP-6-31g(d) differences for SNG-Gx-H geometries optimised at the GFN-xTB and the B3LYP-6-31g(d) level. The colour code is LUMOs, HOMOs and gaps. All values in eV.

| SNG-Gx-H | (B3LYP-6-31g(d)/GFN-xTB) - (B3LYP-6-31g(d)) |
|----------|-----------------------------------------------|
| G0       | -0.04 -0.04 -0.05 -0.01 0.02 -0.01 -0.01 -0.01 0 -0.01 -0.01 -0.01 -0.01 -0.01 -0.01 0.02 0.02 0.02 -0.01 -0.01 -0.04 -0.01 -0.02 -0.01 0.02 0.02 0.03 |
Table S4. TRMC of **SNG-G₀**, **SNG-G₁** and **SNG-G₂** (*λ* = 355 nm, *I₀* = 9.1 x 10^{15} photons/cm²).

| WL [nm] | Power [10⁻² W] | F [10⁻⁴ m²] | Decay | Manual | Average | φΣµ_{Max} [10⁻⁹ m² V⁻¹ s⁻¹] | Δσ_{Max} [10⁻⁷ S cm⁻¹] | Half-lifetime [10⁻⁷ s] |
|---------|----------------|-------------|--------|---------|---------|-----------------------------|------------------------|-----------------------|
| SNG-G₀  | 355 1.00       | 2.57        | 13.9   | 13.7    |         | 10.3                        | 10.1                   | 6.70                  | 0.78                  | 5.92                  |
|         | 355 1.00       | 2.57        | 7.84   | 7.30    | 10.5    | 5.79                        | 5.39                   | 4.64                  | 1.58                  | 3.06                  |
| SNG-G₁  | 355 1.00       | 2.57        | 10.0   | 9.83    | 9.8     | 7.39                        | 7.26                   | 5.90                  | 0.90                  | 5.00                  |
|         | 355 1.00       | 2.57        | 9.80   | 9.70    | 9.7     | 7.24                        | 7.16                   | 9.28                  | 1.29                  | 7.99                  |
| SNG-G₂  | 355 1.00       | 2.57        | 14.2   | 14.1    | 11.1    | 10.5                        | 10.4                   | 6.26                  | 1.01                  | 5.25                  |
|         | 355 1.00       | 2.57        | 8.12   | 8.07    |         | 6.00                        | 5.96                   | 6.01                  | 1.25                  | 4.76                  |
Experimental Procedures

Synthesis and characterisation

Commercial chemicals and solvents were used as received. Analytical thin layer chromatography (TLC) was carried out using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck. Column chromatography was carried out using Silica gel 60 (40-60 µm) from Scharlab. NMR spectra in solution were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometer at 298 K using partially deuterated solvents as internal standards. High Resolution Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) mass spectrometry experiments were recorded in Biomagune in a Ultraspec III (Bruker Daltonics) MALDI-ToF (frequency-tripled (355 nm) Nd:YAG laser) by Dr. Javier Calvo. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on Bruker REFLEX spectrometer in POLYMAT by Dr. Estíbaliz González de San Román Martín. Further evidence of the successful preparation of the SNGs came from MALDI-TOF HRMS that show ion peak masses \((M+\text{Ag})^+\) of 1553.5692, 4211.1790, and 6868.7884 Da, respectively for SNG-G\(_0\), SNG-G\(_1\) and SNG-G\(_2\), that matched with the expected mass. The isotopic distributions could be only recorded for SNG-G\(_0\) and SNG-G\(_1\) due to the high molecular weight of SNG-G\(_2\), which is at the detection limit of the technique that illustrates the extremely high molecular weight of these monodisperse systems.

Steady-state electronic absorption

Absorption spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer.

Photoluminescence

Photoluminescence spectra were recorded on a LS55 Perkin-Elmer Fluorescence spectrometer.

Electrochemistry

Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with glassy carbon disc working electrode, a platinum wire counter electrode and a silver wire pseudoreference electrode. All the potential values are reported versus the redox potential of the ferrocene/ferrocenium couple.

Time-resolved microwave conductivity (TRMC)

A film on a quartz substrate was set in a resonant cavity and probed by continuous microwaves at ~9.1 GHz. The third harmonic generation (THG; 355 nm) of an Nd:YAG laser (Continuum Inc., Surelite II, 5-8 ns pulse duration, 10 Hz) was used as an excitation source (incident photon density, \(I_0 = 9.1 \times 10^{15}\) photons cm\(^{-2}\) pulse\(^{-1}\)). The photoconductivity transient \(\Delta \sigma\) was converted to the product of the quantum yield \((\phi)\) and the sum of the charge carrier mobilities, \(\Sigma \mu = (\mu_h + \mu_e)\) by \(\phi \Sigma \mu = \Delta \sigma (eI_0F_{\text{light}})^{1}\),
where e and $F_{\text{light}}$ are the unit charge of a single electron and the correction (or filling) factor, respectively.
Synthesis of compound C.

Compound A (45 mg, 0.045 mmol) and cyclohexane-1,2,3,4,5,6-hexaone (5 mg, 0.015 mmol) were dissolved in chloroform (9 mL) and acetic acid (3 mL) was added and the reaction was refluxed for 72 hours. Water was added and the product was extracted with chloroform (3 x 25 mL). The organic phase was dried over sodium sulfate, filtrated and removed by rotary evaporation. The crude was loaded onto a chromatographic column (eluent mixture chloroform:toluene 1:3). The solvent was removed under vacuum. Then, the resulting solid was dissolved in chloroform (3 mL) and MnO₂ (10 mg) was added to the solution was stirred for 1 hour. The brown solid was precipitated several times using a mixture of solvents dichloromethane and methanol, the product was obtained pure as bright brown solid (5 mg, 15 %).

¹H-NMR (400 MHz, CDCl₃): 9.53 (d, J = 2.1 Hz, 4H), 8.22 (d, 4H), 4.43 – 4.32 (br s, 8H), 3.91 – 3.75 (br s, 8H), 2.26 – 2.12 (m, 12H), 1.62 (s, 36H), 1.17 (d, J = 6.5 Hz, 72H); ¹³C-NMR (100 MHz, CDCl₃): 177.59, 152.23, 146.29, 144.95, 143.56, 143.12, 132.72, 129.15, 127.57, 127.19, 125.21, 124.73, 116.95, 101.08, 93.28, 61.75, 35.53, 31.67, 26.59, 25.28, 25.06; MS (MALDI, pos.) (m/z): [M+H]⁺ calcd. for C₁₃₀H₁₆₉N₉O₁₀Si₄: 2115.206, found: 2115.013.
Synthesis of SNG-G$_6$

A solution of hexaaminobenzene (340 mg, 2.021 mmol) and 2,7-di-tert-butyl-10,11-dihydro-8b,12a-(epoxyethanoxy)pyreno[4,5-b][1,4]dioxine-4,5-dione (2.339 g, 5.056 mmol) in acetic acid (30 mL) was stirred at 100 °C under nitrogen for 16 h. The reaction was cooled down at room temperature and poured into water (50 mL) and stirred 30 minutes. The precipitate was filtrated and washed with water and methanol. The crude mixture was purified by chromatography column (silica gel dichloromethane/petroleum ether 7:3 and then dichloromethane 100 %) obtaining 1.33 g (45%) of a yellow solid.

$^1$H-NMR (400 MHz, CDCl$_3$): 9.90 (6H, $J = 2.0$ Hz, d), 8.33 (6H, $J = 2.0$ Hz, d), 4.43 (12H, br s), 3.91 (12H, br s), 1.73 (54H, s); $^{13}$C-NMR (400 MHz, CDCl$_3$) 151.84, 143.36, 142.15, 132.43, 129.81, 126.89, 125.66, 124.27, 93.77, 61.99, 35.82, 32.30; MS (MALDI, pos.) ($m/z$): [M+Ag]$^+$ calcd. for C$_{90}$H$_{90}$AgN$_6$O$_{12}$: 1553.5668, found: 1553.5692.
Synthesis of SNG-G\textsubscript{0}-Q

\textbf{SNG-G\textsubscript{0}} (124 mg, 0.086 mmol) was dissolved in a mixture of TFA/water (10 mL, 9:1) at 0 °C. The solution was stirred overnight at room temperature. The precipitate formed was filtrated and washed with water and hot methanol to get 70 mg (69\%) of a yellow solid.

$^1$H-NMR (500 MHz, TFA-d\textsubscript{1}): 10.62 (6H, J = 2.0, d), 9.48 (6H, J = 2.0 Hz, d), 2.28 (54H, s); $^{13}$C-NMR (125 MHz, TFA-d\textsubscript{1}): 183.89, 157.76, 145.61, 143.18, 135.78, 134.88, 132.63, 131.84, 131.21, 38.27, 33.03; MS (MALDI, pos.) (m/z): [M+Ag]$^+$ calcd. for C\textsubscript{78}H\textsubscript{66}AgN\textsubscript{6}O\textsubscript{6}: 1289.4095, found: 1289.4093.
Synthesis of SNG-$G_1$

Compound $A$ (106 mg, 0.105 mmol) and compound $SNG-G_0-Q$ (25 mg, 0.021 mmol) were dissolved in chloroform (3 mL), acetic acid (1 mL) was added and the reaction was refluxed for 72 hours. Water was added and the product was extracted with chloroform (3 x 25 mL). The organic phase was dried over sodium sulfate, filtrated and removed by rotary evaporation. The crude was loaded onto a chromatographic column (eluent mixture chloroform:toluene 3:1). The resulting solid was precipitated in dichloromethane and methanol and the product was obtained as a bright red solid (27 mg, 32%).

$^1$H-NMR (400 MHz, CDCl$_3$): 10.46 (6H, s), 10.20 (6H, $J = 2.0$ Hz, s), 9.60 (6H, $J = 2.0$ Hz, s), 8.24 (6H, s), 4.49 – 4.32 (12H, br s), 3.98 – 3.79 (12H, br s), 2.27 – 2.11 (18H, m), 2.06 (54H, s), 1.67 (54H, s), 1.16 (144H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$): 151.86, 151.33, 144.78, 144.60, 143.70, 142.45, 142.21, 142.14, 132.43, 129.74, 129.61, 129.57, 127.13, 127.04, 126.74, 126.55, 126.31, 124.74, 121.90, 112.58, 102.52, 93.46, 61.76, 36.18, 35.56, 32.75, 31.80, 26.56, 25.31, 25.23; MS (MALDI, pos.) ($m/z$): [M+Ag]$^+$ calcd. for $C_{264}H_{318}AgN_{18}O_{12}Si_6$: 4211.2579, found: 4211.1790.
Synthesis of SNG-G₂

SNG-G₁ (10 mg, 2.43 µmol) was dissolved in TFA (3 mL) and water (1 mL) was added. The reaction was stirred at room temperature and followed by thin layer chromatography. Aqueous work-up was carried out and extracted with chloroform. The organic phase was dried over sodium sulfate anhydrous, filtered and removed by rotary evaporation. The red solid was filtered through a silica plug and used in the next step without further purification. The resulting red solid was dissolved in chloroform (3 mL) and acetic acid (1 mL) and compound A (14 mg, 14 µmol) was added. The reaction was refluxed for 72 hours. The crude was diluted with chloroform and washed with water (3 x 25 mL). The organic phase was dried over sodium sulfate anhydrous, filtered and eliminated by rotary evaporation. The solid was loaded onto a chromatographic column (eluent mixture chloroform:toluene 4:1). The resulting solid was precipitated in dichloromethane and methanol. The product was obtained as a bright pink solid (6 mg, 38%).

^1H-NMR (500 MHz, CDCl₃): 10.55 – 10.43 (6H, m), 10.28 – 10.18 (6H, m), 10.13 – 9.91 (12H, m), 9.65 – 9.49 (6H, m), 8.29 – 8.16 (6H, m), 4.49 – 4.28 (12H, br s), 3.99 – 3.75 (12H, br s), 2.37 – 2.11 (36H, m), 2.09 (54H, s), 1.92 (54H, s), 1.66 (54H, s), 1.30 – 1.07 (m, 288H); ^13C-NMR (125 MHz, CDCl₃): 151.86, 151.35, 151.05, 144.92, 144.87, 144.63, 144.59, 143.74, 143.65, 142.50, 142.42, 142.37, 142.10, 132.41, 129.73, 129.69, 129.62, 127.37, 127.12, 126.82, 126.32, 125.44, 124.76, 122.00, 121.80, 121.86, 121.80, 112.90, 112.81, 112.61, 112.55, 112.41, 102.50, 102.46, 102.39, 93.45, 61.79, 36.22, 35.99, 35.55, 32.78, 32.37, 31.80, 27.27, 26.60, 26.53, 25.37, 25.29, 25.17; MS (MALDI, pos.) (m/z): [M+Ag]^+ calcd. for C_{438}H_{546}Ag_{30}N_{30}O_{12}Si_{12}: 6868.0154, found: 6868.7884.
Figure S6. $^1$H NMR of the compound C in CDCl$_3$. 
Figure S7. $^{13}$C NMR of the compound C in CDCl$_3$. 
Figure S8. MALDI-TOF of the compound C.
Figure S9. $^1$H NMR of the compound SNG-G$_0$ in CDCl$_3$. 
Figure S10. $^{13}$C NMR of the compound SNG-G$_0$ in CDCl$_3$. 
Figure S11. MALDI-TOF of the compound SNG-G$_0$. 
Figure S12. $^1$H NMR of the compound SNG-G$_0$-Q in TFA-$d_1$. 
Figure S13. $^{13}$C NMR of the compound SNG-G$_0$-Q in TFA-$d_1$. 
Figure S14. MALDI-TOF of the compound SNG-G₀-Q.
Figure S15. $^1$H NMR of the compound SNG-G₁ in CDCl₃.
**Figure S16.** $^{13}$C NMR the compound **SNG-G$_1$** in CDCl$_3$.
Figure S17. MALDI-TOF of the compound SNG-G₁.
Figure S18. $^1$H NMR of the compound SNG-G$_2$ in CDCl$_3$. 
Figure S19. $^{13}$C NMR the compound SNG-G$_2$ in CDCl$_3$. 
Figure S20. MALDI-TOF of the compound SNG-G₂.
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