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Supramolecular polymers have a lot of potential in the development of new materials because of their inherent recyclability and their self-healing and stimuli-responsive properties. Supramolecular conductive polymers are generally obtained by the assembly of individual disk-like π -conjugated molecules into columnar arrays that provide an optimal channel for electronic transport. We report a new approach to prepare supramolecular polymers by hooking together sigmoidal monomers into 1D arrays of π -stacked anthracene and acridine units, which give rise to micrometer-sized fibrils that show pseudoconductivities in line with other conducting materials. This approach paves the way for the design of new supramolecular polymers constituted by acene derivatives with enhanced excitonic and electronic transporting properties.

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Hooking Together Sigmoidal Monomers into Supramolecular Polymers

Marco Carini,^[a] Mauro Marongiu,^[a] Karol Strutyński,^[b] Akinori Saeki,^[c] Manuel Melle-Franco,^[b] and Aurelio Mateo-Alonso^{*[a][d]}

Abstract: Supramolecular polymers have a lot of potential in the development of new materials because of their inherent recyclability and their self-healing and stimuli-responsive properties. Supramolecular conductive polymers are generally obtained by the assembly of individual disk-like π -conjugated molecules into columnar arrays that provide an optimal channel for electronic transport. We report a new approach to prepare supramolecular polymers by hooking together sigmoidal monomers into 1D arrays of π -stacked anthracene and acridine units, which give rise to micrometer-sized fibrils that show pseudoconductivities in line with other conducting materials. This approach paves the way for the design of new supramolecular polymers constituted by acene derivatives with enhanced excitonic and electronic transporting properties.

Supramolecular polymers play a pivotal role in materials science because of their inherent recyclability and their self-healing and stimuli-responsive properties.^[1-2] Such properties are a direct consequence of their non-covalent nature and of the reversibility of the monomer to polymer equilibrium. Furthermore, the high directionality of non-covalent interactions, such as hydrogen bonds or π -stacking allows constructing ordered and shape-persistent nanometric and even micrometric polymeric assemblies with high precision by spontaneous self-assembly of molecular monomers.^[3-4]

All the above-mentioned features make supramolecular polymers an ideal platform to develop materials for electronic applications, since efficient electronic transport is dominated by the precise spatial organization of organic semiconductors. For instance, lamellar π -stacking has been identified as an optimal molecular arrangement for electronic transport since it favours intermolecular electronic coupling.^[5-17] Most supramolecular polymers for electronic applications involve the assembly of individual disk-like π -conjugated molecules (through hydrogen bonding, solvophobic, π -stacking and/or CT interactions) into columnar arrays in order to open an optimal channel for electronic transport.

Scheme 1. Synthesis and structure of supramolecular polymer (**Ac-A-Ac**)_n.

Herein, we report a new family of supramolecular (**Ac-A-Ac**)_n polymers that are obtained by hooking sigmoidal **Ac-A-Ac** monomers into a one-dimensional array of stacked anthracene (A) and acridine (Ac) units (Scheme 1). The **Ac-A-Ac** monomers are constituted by two external acridine units stitched to a central anthracene unit by 2,6-pyridinedicarboxamides. First, the **Ac-A-Ac** monomers fold into a sigmoidal hook-like conformation by intramolecular hydrogen bonds between the amides and the pyridinic nitrogen that gives rise to two adjacent antiparallel cavities of ~ 7 Å. Then, the folded **Ac-A-Ac** monomer can be hooked into another folded **Ac-A-Ac** monomer by hydrogen bonds between the acridine nitrogen of one monomer and the amides of another monomer and by π -stacking. This monomer assembly mode leaves always two available cavities that promote the incorporation of additional monomers and therefore the formation of supramolecular (**Ac-A-Ac**)_n polymers. In fact, the **Ac-A-Ac** monomers spontaneously self-assemble to provide

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micrometer long nanofibers with charge transporting properties similar to those of conducting polymers.

In addition to the self-assembling structural features described above, anthracene and acridine units were selected because of their excellent structural and electronic complementarity since they are constituted by three linearly fused rings and also because of their well-balanced properties in terms of charge transport, stability and solubility. Also, triisopropylsilyl (TIPS) groups have been introduced in the pyridine units to increase the solubility. To ensure that the **Ac-A-Ac** monomers are able to self-assemble into desired **(Ac-A-Ac)_n** polymers, a series of model experiments were carried out with **A-A** and **Ac-A** tweezer-like compounds (Figures 1 and 2) in order to understand the interactions between the different units and motifs. **A-A** has been prepared following a route described previously by some of us,^[18] while all details of the synthesis and characterization of the **Ac-A** and **Ac-A-Ac** are given in the supporting information.

Figure 1. A) Scheme showing the assembly process between **A-A** and 9-methylacridine. B) ¹H-NMR of **A-A** (5 × 10⁻³ M, 25 °C) in TCE-d₂ (red); ¹H-NMR of **A-A** (5 × 10⁻³ M, 25 °C) with an excess (6 eq) of 9-methylacridine in TCE-d₂ (blue); ¹H-NMR of 9-methylacridine in TCE-d₂ (black). The asterisks indicate residual solvent peaks.

To ensure that acridines able to self-assemble into the cavity of the folded **Ac-A-Ac** monomers, the supramolecular interaction between 9-methylacridine into the model **A-A** tweezers was studied (Figure 1). The NMR spectrum of a mixture of **A-A** in the presence of an excess of 9-methylacridine shows that the amide NH signals of **A-A** are deshielded in comparison to those of the

free **A-A**, which is consistent with the formation of hydrogen bonds with the nitrogen of acridine. Furthermore, the anthracene signals (A, A', B and B') and the 9-methylacridine signals (1, 2, 3 and 4) in the mixture are shielded in comparison to those of free **A-A** and free 9-methylacridine, respectively. These changes can be explained in terms of anisotropy because of the close proximity of the anthracene and acridine units as the result of π -stacking. NMR titration of **A-A** with increasing amounts of 9-methylacridine in 1,1,2,2-tetrachloroethane-d₂ (TCE-d₂) (Figure S1) also evidenced similar changes in the NMR spectra consistent with the formation of the complex. From the titration experiments, an association constant (K_a) of $1.4 \times 10^2 \text{ M}^{-1}$ was estimated.^[19-21]

One of the key steps in the formation of the **(Ac-A-Ac)_n** polymers rely on the formation of an assembly with four interacting anthracene and acridine units held together by two sets of intermolecular hydrogen bonds. Again, to ensure that the formation of such multimode assembly is possible, a model **Ac-A** tweezer that shows exactly the same self-recognition pattern as **Ac-A-Ac** but that upon self-assembly will evolve into the **(Ac-A)₂** dimer rather than into the **(Ac-A-Ac)_n** (Figure 2). To evaluate the homodimerisation of the **Ac-A**, ¹H NMRs in different solvents were recorded at different concentrations. The ¹H NMR spectrum recorded in dimethylsulfoxide-d₆ (DMSO-d₆) show the individualised (undimerised) **Ac-A** since the aromatic signals (A, B, C, D, G and H) resonate all at the typical chemical shift values of anthracene and acridine derivatives (8.5–7.4 ppm) in this solvent. This is because of the high hydrogen bond basicity of DMSO disturbs the intermolecular hydrogen bond, favouring solvation rather than dimerization. The ¹H NMR spectrum of **Ac-A** recorded in TCE-d₂, a solvent with a low hydrogen bond basicity that does not interfere with the hydrogen bonds, evidence the homodimerization of **Ac-A** into **(Ac-A)₂**. In fact, the NH signals resonate at chemical shifts consistent with the formation of hydrogen bonds (10.09 and 9.46 ppm). Moreover, the anthracene and acridine signals are broadened and appear strongly shielded (at 7.6–6.6 ppm) as an effect of anisotropy that support π -stacking. The ability of **Ac-A** to dimerise is also evidenced by matrix-assisted laser desorption ionization (coupled to a time-of-flight analyser) mass spectrometry (MALDI-TOF MS) that shows the $[2M+Na]^+$ mass peak corresponding to **(Ac-A)₂** in the gas phase, besides the $[M+H]^+$ and $[M+Na]^+$ ions (Figure S2).

The homodimerization features in the ¹H NMR spectra are persistent upon dilution down to the NMR detection limit ($\sim 10^{-4} \text{ M}$), which indicate that the dimerization constant (K_d) is $>10^4$ (Figure S3). To overcome this, K_d was estimated by means UV-vis spectroscopy through dilution experiments from 10^{-4} to 10^{-6} M (Figure S4). By this method, a dimerization constant $K_d = 8.56 \times 10^5 \text{ M}^{-1}$ was estimated,^[19-21] which is almost four orders of magnitude higher than the constant of the **Ac@A-A** complex.

Figure 2. A) Scheme showing the dimerisation of **Ac-A**. B) ¹H-NMR of **Ac-A** (80 °C) in DMSO-*d*₆ (red) and of **Ac-A** (25 °C) in TCE-*d*₂ (blue). The asterisks indicate residual solvent peaks.

The studies on the model compounds evidenced that the **Ac-A-Ac** monomer will be able to self-assemble in a similar fashion to **Ac-A** but providing two cavities that will enable the inclusion of additional monomers to provide **(Ac-A-Ac)_n** (Scheme 1). In contrast to **Ac-A**, the **Ac-A-Ac** monomer was only found to be soluble during chromatographic purification from the crude mixture. Remarkably, after evaporating the solvent (chloroform) from the fractions containing **Ac-A-Ac**, a virtually insoluble material was obtained that could not be re-dissolved in any chlorinated solvent. This irreversible change of solubility of the **Ac-A-Ac** monomer is consistent with the formation of the **(Ac-A-Ac)_n** supramolecular polymer upon the evaporation of the solvent. Definitive evidence of the formation of the **(Ac-A-Ac)_n** polymer came from atomic force microscopy (AFM) and scanning electron microscopy (SEM). The AFM and SEM images of the **(Ac-A-Ac)_n** dispersions in TCE revealed the presence of fibrils with a thickness of 20–40 nm that extend in length over several micrometers (Figures 3 and S5–S8). While the images of the deposited samples of **Ac-A** using the same conditions showed an unstructured film-like coverage of the surface with no evident morphology (Figure S9). This is consistent with the fact that **Ac-A** can only dimerise and not polymerise.

Figure 3. Morphology of the **(Ac-A-Ac)_n** supramolecular polymer. A) AFM on mica 10x10 μm. B) AFM on mica 2.5x2.5 μm. C) SEM on holey carbon film coated copper grid 2.5x2.5 μm.

The **(Ac-A-Ac)_n** can be disassembled into smaller oligomers and even into monomers by increasing the temperature or by using solvents with a high hydrogen bond basicity. For instance, the **(Ac-A-Ac)_n** polymer can be partially disassembled at high temperatures into smaller oligomers as illustrated by VT-NMR experiments in TCE-*d*₂, where the broad signals in the aromatic region split into partially resolved signals that resonate at the chemical shifts expected for the acridine and anthracene units (Figure S10). Also, **(Ac-A-Ac)_n** polymer could be completely dissolved in trifluoroacetic acid (TFA) that strongly disturbs the hydrogen bonds and protonates the acridine nitrogen, as revealed by the ¹H NMR in TFA-*d*₁, where structure of the disassembled **Ac-A-Ac** monomer was observed (Figure S11).

The intrinsic charge transport properties of the **(Ac-A-Ac)_n** polymer were evaluated by means of flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements. This method measures directly the pseudoconductivity (defined as $\phi\Sigma\mu$, where ϕ and $\Sigma\mu$ are the photocarrier-generation yield and the sum of the mobilities of the generated charge carriers, respectively) without introducing electrodes. The $\phi\Sigma\mu$ maxima can be considered the minimum mobility of the material since the ϕ values are submultiples of the unit. A pseudoconductivity value $\phi\Sigma\mu = 2.40 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was estimated for the **(Ac-A-Ac)_n** polymer from the resultant rise and decay profiles of transient conductivities (Figure 4A). These $\phi\Sigma\mu$ values are in line with other conducting materials such as nanographenes,^[22–23] stacked pseudorotaxanes,^[24] peropyrene fibers,^[25–26] and conjugated polymers.^[27]

Figure 4. A) TRMC of $(\text{Ac-A-Ac})_n$. B) Frontier orbitals of $(\text{Ac-A-Ac})_n$.

To provide a picture of the electronic structure of **Ac-A-Ac**, theoretical calculations were carried out. For this, we first built a 1D crystal by replicating a suitably oriented molecule containing the aromatic core of **Ac-A-Ac**. Then, we explored configurational space by molecular dynamics and systematic minimizations with different 1D periodic lengths with a semiempirical tight binding model. The best minima found were then studied at the DFT GGA level while orbitals and corresponding energies were obtained with a hybrid Hamiltonian. The electronic structure and the orbitals of the frontier orbitals for the $(\text{Ac-A-Ac})_n$, in which the TIPS groups have been substituted by hydrogen, are qualitatively similar for studied cases (full details can be found in the supporting information). For each extra molecule in the periodic unit cell there is an extra nearly-degenerate HOMO and LUMO level. HOMO orbitals have consistently large densities on the anthracene moieties, while LUMO orbitals have consistently large densities on the two acridine neighbouring moieties (Figures 4B and S12). Remarkably, for all models, the electron densities of the frontier orbitals are spread throughout the stacked anthracene and acridine units, which act as channels for electronic transport.

To conclude, a new approach to prepare supramolecular polymers by hooking together sigmoidal **Ac-A-Ac** monomers into 1D arrays of stacked anthracene and acridine units has been reported. The **Ac-A-Ac** monomers are able to self-assemble by a combination of hydrogen bonds and π -stacking as demonstrated by a series of studies carried out on model compounds that show how **A-A** can complex acridine and **Ac-A** can dimerise, in a similar fashion as the **Ac-A-Ac** monomers. Furthermore, the **Ac-A-Ac** monomers have shown to form $(\text{Ac-A-Ac})_n$ spontaneously giving rise to micrometer-sized fibrils that show pseudoconductivities in

line with other conducting materials. The approach reported here will pave the way for the preparation of supramolecular polymers constituted of acene derivatives, which combine the properties in electronic and excitonic transport and singlet fission of acenes with the recyclability and self-healing properties of supramolecular polymers.

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Figure S1. NMR titration of anthracene dimer (**A-A**) and 9-methylacridine in TCE- d_2 , 500 MHz, 25°C at a constant concentration of **A-A** of 5×10^{-3} . Titrant solution is 5×10^{-2} M of 9-methylacridine in host solution. $K = 139.81 \text{ M}^{-1} \pm 1.1983\%$ is calculated on the variation of chemical shift of protons **B**, **C**, **E**, and **F**.

Figure S2. MALDI-TOF of dyad **Ac-A**. Calculated for $[M+H]^+$: 856.425, found: 856.833; Calculated for $[2M+Na]^+$: 1734.829, found: 1733.450.

Figure S3. $^1\text{H-NMR}$ dilution experiment of **Ac-A** (TCE-d_2 , 500 MHz, 25°C)

Figure S4. Left: UV-Vis dilution experiment of dyad **Ac-A** (TCE, 25°C), Right: normalized at 362 nm

Figure S5. AFM images of polymer **Ac-A-Ac**: 5×10^{-4} M, r.t.

Figure S6. AFM images of polymer **Ac-A-Ac**: 5×10^{-4} M, r.t., annealing on mica surface: 60°C, 15 min.

Figure S7. AFM images of polymer **Ac-A-Ac**: $5 \times 10^{-4} \text{ M}$, $150^\circ \text{C} \rightarrow \text{r.t.}$

Figure S8. AFM images of polymer **Ac-A-Ac**: $5 \times 10^{-5} \text{ M}$, r.t.

Figure S9. AFM images of compound **Ac-A**: 5×10^{-4} M, r.t.

Figure S10. Variable Temperature ^1H -NMR in $\text{TCE-}d_2$ of **Ac-A-Ac**, ($4 \times 10^{-3}\text{M}$) from bottom to top: heating-cooling-heating.

Figure S12. Frontier orbital of two optimized unit cells with two monomers with similar (top) and different (bottom) relative orientations at the B3LYP/light // PBE-MBD/light level.

Materials and Methods

Commercial chemicals and solvents were used as received. Tetrahydrofuran was dried using an Innovative Pure Solve solvent purification system. 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.

Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments MALDI-TOF) were recorded on Bruker REFLEX spectrometer by Dr. Antonio Veloso at POLYMAT.

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

AFM was recorded on a AFM Dimension ICON (Bruker) (Tapping mode, Tips: Tesp-v2 (Spring Const.: 37 N/m, Resonant Freq.: 320 kHz) by Dr. María Dolores Martín Alberdi at the University of the Basque Country. AFM samples were prepared by dissolving / suspending Ac-A-Ac in tetrachloroethane at the concentration and temperature indicated below. 2 drops were deposited on a mica surface and left to evaporate. There is no significant effect of concentration and temperature on the morphology of the fibers.

SEM was recorded on a FEI HELIOS 450S by Dr. Evgenii Modin at CIC NanoGUNE.

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 (ϕ) 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_{light} are the unit charge of a single electron and the correction (or filling) factor, respectively.

Synthesis

Scheme S1. Compounds **2**, **7**, **8** and Anthracene dimer **A-A** were synthesized according to the literature.^[1]

Synthesis of 1

331 μl of 2,4-dimethoxybenzylamine (2.205 mmol) and 384 μl of diisopropylethylamine (2.205 mmol) were dissolved in 6 ml of chloroform. 300 mg of 9-(bromomethyl)acridine (1.102 mmol) were added dropwise at 0°C in 15 ml of chloroform during 1 hour. The reaction was stirred at r.t. for 4 hours and the solvent removed under reduced pressure. The product was purified by column chromatography in $\text{CHCl}_3 \rightarrow \text{CHCl}_3 / \text{MeOH}$ 99:1. The residue was dissolved in few ml of Et_2O and HCl saturated solution in Et_2O was added with stirring. The hydrochloride salt precipitates as a yellow-orange solid, that was filtered and washed with Et_2O . 353.2 mg (0.819 mmol) obtained. 74%

The product was stored at -18°C and used within few days without further purification.

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.53 (s, 2H), 8.56 (d, $J = 9.0$ Hz, 2H), 8.44 (d, $J = 8.9$ Hz, 2H), 8.12 (t, $J = 7.6$ Hz, 2H), 7.88 (t, $J = 7.7$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 1H), 6.64 (s, 1H), 6.58 (d, $J = 8.6$ Hz, 1H), 5.32 (s, 2H), 4.39 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), MS (MALDI): m/z calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 359.175, found 359.029.

A ^{13}C NMR could not be recorded since the compound degrades in solution both as free base in CDCl_3 and as HCl salt in $\text{DMSO}-d_6$.

Figure S13. ¹H-NMR (400 MHz, DMSO-*d*₆) of compound **1**.

Synthesis of 3

1.500 g of **2** (4.149 mmol) were dissolved in 10 ml of DMF, 50 mg of 4-dimethylaminopyridine (0.415 mmol) and 867 μl of triethylamine were added (6.224 mmol), 2.717 g of Boc_2O (12.448 mmol) were added in 5 ml of DMF and the reaction was stirred overnight at r.t. Water was added and the product was extracted with Hexane. The product was purified by flash chromatography in Hexane $\rightarrow$ DCM.

1.3431 g (3.216 mmol) obtained, colorless oil. 78%

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 1.4$ Hz, 1H), 8.16 (d, $J = 1.5$ Hz, 1H), 4.01 (s, 3H), 1.65 (s, 9H), 1.14 (m, 21H), ^{13}C NMR (101 MHz, CDCl_3) δ 165.11, 162.90, 149.88, 148.57, 134.20, 129.79, 129.75, 102.70, 100.21, 83.33, 53.25, 28.17, 18.72, 11.29, MS (MALDI): m/z calcd. for $\text{C}_{23}\text{H}_{35}\text{NO}_4\text{SiNa}$ $[\text{M}+\text{Na}]^+$: 440.223, found 440.319.

Figure S14. ¹H-NMR (400 MHz, CDCl₃) of compound 3.

Figure S15. ¹³C-NMR (100 MHz, CDCl₃) of compound **3**.

Synthesis of 4

1.339 g of **3** (3.207 mmol) were dissolved in 8 ml of THF and 141 mg of NaOH (3.528 mmol) were added in 2 ml of water. The reaction was stirred overnight at r.t., diluted with water and 2M HCl until pH ~ 3 and extracted with CHCl₃. The product was purified by column chromatography in CHCl₃ / MeOH 95:5. 1.0353 g (2.565 mmol) obtained, colorless oil. 80%

¹H NMR (400 MHz, DMSO-d₆) δ 13.71 (bs, 1H), 8.10 (s, 1H), 8.05 (s, 1H), 1.58 (s, 9H), 1.11 (m, 21H), ¹³C NMR (101 MHz, DMSO-d₆) δ 165.00, 162.57, 149.62, 132.25, 128.75, 128.22, 102.83, 98.37, 82.37, 27.60, 18.38, 10.53, MS (MALDI): m/z calcd. for C₂₂H₃₃NO₄SiNa [M+Na]⁺: 426.207, found 426.243.

Figure S16. ¹H-NMR (400 MHz, DMSO-*d*₆) of compound **4**.

Figure S17. ¹³C-NMR (100 MHz, DMSO-*d*₆) of compound 4.

Synthesis of 5

300 mg of **4** (0.743 mmol) were dissolved in 3 ml of dry DCM under N_2 atmosphere and 319 μl of oxalyl chloride (3.717 mmol) were added at 0°C , followed by 2 drops of dry DMF. The solution was left to warm to r.t. and was stirred for 2 hours, then the solvent was removed under reduced pressure and the acid chloride was vacuum-dried for 30 min. The residue was dissolved in 3 ml of dry chloroform under N_2 atmosphere and a solution of 353 mg of **3** (0.818 mmol) and 518 μl of triethylamine (3.717 mmol) in 3 ml of dry chloroform were added at 0°C . The mixture was stirred for 1h30' at r.t. The product was purified by column chromatography in chloroform.

426.0 mg (0.573 mmol) obtained, off-white solid. 77%

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.7$ Hz, 2H), 8.11 (d, $J = 9.0$ Hz, 2H), 7.98 (s, 1H), 7.87 (s, 1H), 7.76 (t, $J = 7.7$ Hz, 2H), 7.48 (t, $J = 7.7$ Hz, 2H), 6.93 (d, $J = 8.4$ Hz, 1H), 6.26 (d, $J = 8.4$ Hz, 1H), 6.06 (s, 1H), 5.81 (s, 2H), 4.30 (s, 2H), 3.76 (s, 3H), 3.16 (s, 3H), 1.47 (s, 9H), 1.13 (d, $J = 4.2$ Hz, 21H), ^{13}C NMR (101 MHz, CDCl_3) δ 168.52, 163.58, 160.42, 157.97, 154.50, 148.70, 133.67, 130.11, 129.45, 128.54, 127.40, 126.29, 124.64, 116.49, 104.09, 103.11, 98.09, 82.55, 55.53, 54.51, 45.48, 39.77, 28.08, 18.74, 11.32, MS (MALDI): m/z calcd. for $\text{C}_{45}\text{H}_{54}\text{N}_3\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 744.382, found 744.640.

Figure S18. ^1H -NMR (400 MHz, CDCl_3) of compound **5**.

Figure S19. ^{13}C -NMR (100 MHz, CDCl_3) of compound **5**.

Figure S20. HH-COSY (400 MHz, CDCl₃) of compound **5**.

Synthesis of Ac-A-Ac

799.4 mg of **5** (1.074 mmol) were dissolved in 20 ml of TFA, the reaction was stirred at r.t. for 2 hours and the solvent was removed under reduced pressure. The product was suspended in Et₂O, filtered and washed with Et₂O, re-suspended in Toluene, filtered and washed with few ml of Tol, re-suspended in Acetone, filtered, washed with Acetone and Et₂O.

577.1 mg (599.9 mmol) obtained, white powder. 82% (~80% purity by NMR)

(**6**) ¹H NMR (400 MHz, TFA-d) δ 9.18 (d, *J* = 8.9 Hz, 2H), 8.86 (dd, *J* = 8.6, 1.5 Hz, 2H), 8.75 – 8.61 (m, 4H), 8.36 (dd, *J* = 8.3, 1.8 Hz, 2H), 6.39 (s, 2H) 1.73 – 1.28 (m, 21H), MS (MALDI): *m/z* calcd. for C₃₂H₃₆N₃O₃Si [*M*+H]⁺: 538.252, found 538.406.

The product was used in the next step without further purification.

165 mg of **6** (0.2539 mmol) and 43 mg of HOBT·H₂O (0.3174 mmol) were vacuum-dried and suspended in 15 ml of dry chloroform under nitrogen atmosphere. 53 mg of EDC·HCl (0.2793 mmol) were added at 0°C, the mixture was stirred at 0°C for 2 hours. 30 mg of **7** (0.1270 mmol) were added, followed by 177 μl of triethylamine (1.2695 mmol) and the mixture was allowed to warm to room temperature and stirred overnight with protection from light. The crude of reaction was adsorberd on celite and loaded into a column chromatography and eluted with DCM → CHCl₃ (containing 0.6% of EtOH). The chromatographic separation has to be repeated and the product was finally triturated with MeOH.

39.9 mg (0.0313 mmol) obtained, yellow solid. 25%

¹H NMR (400 MHz, TFA-d) δ 8.71 (d, *J* = 9.0 Hz, 4H), 8.31 (d, *J* = 9.4 Hz, 4H), 8.29 – 8.13 (m, 12H), 7.84 (t, *J* = 7.7 Hz, 4H), 7.52 (dd, *J* = 7.1, 3.2 Hz, 4H), 5.90 (s, 2H), 5.78 (s, 2H), 1.19 – 0.88 (m, 42H), ¹³C NMR (126 MHz, TFA) δ 155.93, 147.24, 146.56, 144.14, 141.53, 140.66, 132.67, 131.72, 131.03, 130.93, 129.64, 129.37, 127.80, 127.65, 126.10, 122.06, 102.79, 40.11, 38.76, 19.21, 12.96. MS (MALDI): *m/z* calcd. for C₈₀H₈₃N₈O₄Si₂ [*M*+H]⁺: 1275.607, found 1276.033

Figure S21. ^1H -NMR (400 MHz, TFA-d) of compound **Ac-A-Ac**.

Figure S22. ¹H-NMR (400 MHz, TFA-*d*) of compound **Ac-A-Ac**.

Figure S23. HH-COSY (400 MHz, TFA-*d*) of compound **Ac-A-Ac**.

Synthesis of Ac-A

50.0 mg of **6** (0.767 mmol, ~80% purity) and 22.8 mg of HOBT·H₂O (0.1688 mmol) were vacuum-dried for 30 minutes and then suspended in 5 ml of dry CHCl₃ under nitrogen atmosphere. 32.4 mg of EDC·HCl (0.1688 mmol) were added at 0°C, the mixture was stirred at 0°C for 2h, then 71.5 mg of **7a** (0.1918 mmol) were added to the reaction, followed by 80 µl of triethylamine (0.5754 mmol). The mixture was allowed to warm to r.t. and was stirred overnight with protection from light. The reaction was diluted with CHCl₃ and washed with water and BRINE. The organic phase was evaporated and the residue was suspended in 5 ml of AcOH and filtered, the precipitate was washed with AcOH until it remains white and all the yellow product passed in the filtrate (3x5 ml). The solution was diluted with CHCl₃ and washed with water, saturated NaHCO₃ solution and BRINE. The product was purified by column chromatography in CHCl₃ → CHCl₃ / MeOH 99:1 and was finally precipitated from CHCl₃ to MeOH.

17.1 mg obtained (light yellow solid). 26%

¹H NMR (500 MHz, DMSO-d₆, 80°C) δ 9.44 (t, *J* = 6.1 Hz, 1H, NH), 9.18 (t, *J* = 6.1 Hz, 1H, NH), 8.51 (d, *J* = 8.9 Hz, 6H), 8.14 (d, *J* = 8.8 Hz, 2H), 8.12 (s, 1H), 8.07 (s, 1H), 7.79 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.55 (dd, *J* = 9.0, 6.4 Hz, 2H), 7.45 – 7.35 (m, 4H), 6.95 (bs, 1H, NH), 5.52 (d, *J* = 5.7 Hz, 2H), 5.50 (d, *J* = 5.9 Hz, 2H), 5.19 (d, *J* = 5.6 Hz, 2H), 1.42 (s, 9H), 1.21 – 1.05 (m, 21H). ¹³C NMR (126 MHz, DMSO-d₆, 80°C) δ 162.21, 161.92, 149.18, 149.04, 147.90, 140.20, 132.60, 129.61, 129.29, 125.50, 125.13, 124.99, 124.77, 124.55, 124.48, 102.88, 98.28, 36.42, 35.47, 34.70, 27.85, 17.90, 10.26. MS (MALDI): *m/z* calcd. for C₅₃H₅₈N₅O₄Si [M+H]⁺: 856.425, found 856.833, C₅₃H₅₇N₅O₄SiNa [M+Na]⁺: 878.407, found 878.805, C₁₀₆H₁₁₄N₁₀O₈Si₂Na [2M+Na]⁺: 1733.825, found 1733.450.

Figure S24. ^1H -NMR (500 MHz, $\text{DMSO}-d_3$, 80°C) of compound **Ac-A**.

Figure S25. ¹³C-NMR (125 MHz, DMSO-*d*₆, 80°C) of compound **Ac-A**.

Figure S26. Structure of **Ac-A-Ac** monomer chemical structure (top), and 3D atomic view in the polymerizable conformation, side (bottom left) and top (bottom right) views.

Figure S27. Polymerization of **Ac-A-Ac** represented in 3D form (top) and as an idealized scheme (bottom). Aromatic core molecule (without triisobutylsilyl groups) as modelled (**Ac-A-Ac'**).

Density Functional Tight Binding Models

A Semi-empirical, Density Functional Theory Tight Binding (DFTB), Hamiltonian was used as a fast, yet relatively accurate alternative to DFT to screen and probe different possible conformations of the polymer. For this, 1D periodic structures with one and two molecules per unit cell were optimized using the 3OB parameter set with vdW empirical corrections with and without a hydrogen bonding term, DFTB-D3H5 and DFTB-D3 respectively. In order to ensure that interactions between cells could be neglected, the cell box sides were set to 50 Å. The hydrogen-bond corrected Hamiltonian showed slightly larger unit cells and larger binding energies, Table S1. We performed MD to explore configurational space and try to reach the most representative minima possible. This procedure found an almost isoenergetic minimum (difference lower than chemical accuracy) where the two monomer molecules in the unit cell present different relative orientations, Figure S28.

		Total Energy	1D Periodicity	Band Gap	Intermolecular Energy
	Monomers / UC	eV	Å	eV	kcal/mol
3OB/DFT-D3	1	-4201.362	9.976	1.844	---
3OB/DFT-D3	2	-8402.728	19.908	1.850	-132.868
3OB/DFT-D3H5	1	-4198.703	10.113	1.683	---
3OB/DFT-D3H5	2	-8397.405	20.179	1.686	-153.398
3OB/DFT-D3H5 (after MD)*	2	-8397.563	19.837	1.498	-154.317

Table S1. DFTB+ optimization of 1D polymers with 1 and 2 monomers per unit cell. *: best minimum obtained after MD simulations.

Figure S28. Best minimum (after MD simulations) top (left) and side (right) views.

Figure S29. Energy difference at the 3OB/DFTB-D3H5 level as a function of unit cell length.

DFT Models (Geometries)

Density Functional Theory (DFT) was used to improve and confirm the DFTB findings. Models were computed with the Fritz Haber Institute *ab initio* molecular simulations (FHI-aims) package^[2-4] utilizing "light" numeric atomic orbitals. These atomic orbitals set approximately correspond to a TZVP Gaussian basis set. Two functionals, PBE and BLYP, were tried for geometry optimization, while the B3LYP functional was used to compute HOMO-LUMO gaps and frontier orbitals. Dispersion interactions are fundamental for a proper description of the stacking of acridines and anthracene. PBE and BLYP functionals were augmented with Tkatchenko-Scheffler^[5] and Many-body van der Waals^[5] corrections, -vdW or -MBD, respectively. The minima geometries were considered converged after the maximum atomic force was below 0.002 eV/Å, as lower values were not easy to achieve due to the presence of spurious small forces from neighbouring unit cells. Remarkably the binding energies are similar to what computed with DFTB, and the same minimum is found with similar energetic differences, thus confirming the accuracy of the findings at the DFTB level.

method (// geometry)	Monomers / UC	Total Energy	1D Periodicity	Band Gap	Intermolecular Energy
		eV	Å	eV	kcal/mol
BLYP-vdW	1	-85108.863	9.825	1.776	
BLYP-vdW	2	-170217.728	19.663	1.650	
PBE-MBD	1	-85019.595	10.614	1.678	
PBE-MBD	2	-170039.207	21.074	1.620	-122.442
PBE-MBD (after MD)*	2	-170039.300	20.631	1.525	-123.191
B3LYP // PBE-MBD	1	-85113.899	10.614	2.801	
B3LYP // PBE-MBD	2	-170227.720	21.074	2.742	
B3LYP // PBE-MBD (after MD)*	2	-170227.755	20.633	2.637	

Table S2. BLYP-vdW and PBE-MBD geometry optimizations and B3LYP values on PBE-MBD with the light numerical orbitals.

*: Best minimum obtained after MD simulations at the DFTB level.

Figure S30. Energy difference at the PBE-MBD/light level as a function of unit cell length.

DFT Models (Frontier Orbitals)

The frontier orbitals were computed in order to understand how frontier electrons are distributed in the polymeric material at the band gap energies. Although a monomer 1D unit cell represents properly a structural minimum, it was found that at least two points in reciprocal space were needed to convergence the total energy. Considering this, to check the accuracy of the electron distribution computed in real space, unit cells with 1, 2 and 3 monomers were computed at the Γ -point at the B3LYP level and compared, Figure S31. Larger cells were made by replication of the monomer unit cell structure computed at the PBE-MBD level. This comparison shows that although most features for frontier electrons for all the three systems are common for the three systems, some small differences can be observed in some densities for the monomer. This shows, that electronically, real space calculations need at least two monomers in the unit cell to be accurate. In addition, we compared orbitals for the two isoenergetic two monomer unit cells minimized at the PBE-MBD level, Figure S12. Although the degeneracy is lifted due to the more extended asymmetry, the fundamental features of the frontier orbitals are preserved.

Figure S31. Frontier orbitals of one monomer (top), two monomers (center) and three monomers (bottom) unit cells constructed by replication of the monomer PBE-MBD/light structure computed with a B3LYP/light Hamiltonian. Frontier orbitals are marked by boxes.

Author Contributions

M.C. developed the synthetic route and performed the characterizations and the titrations; M.M. synthesized the precursors and the polymer in larger scale; K.S. and M.M.-F. performed the theoretical calculations; A.S. carried out the TRMC measurements and interpreted the data; M.C. and A.M.-A wrote the paper with the input from all authors; A.M.-A. conceived and supervised the study.

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