Supporting Information

Doubling the Length of the Longest Pyrene-Pyrazinoquinoxaline Molecular Nanoribbons

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Figure S1. Bond length analysis and NICS(0) values of NR-20-H, NR-40-H, NR-60-H. Bonds are rendered in a color continuum ranging from red (1.31 Å) to white (1.40 Å) to blue (1.49 Å) so that Clar’s aromatic sextets are lighter-whiter colors and localized double and single bonds are red and blue, respectively.
Figure S2. ACID plots of NR-20-H and NR-40-H.
Figure S3. Frontier orbitals of NR-20-H.
Figure S4. Frontier orbitals of NR-40-H.
Figure S5. Frontier orbitals of NR-60-H.
Figure S6. TD-DFT calculated electronic absorption spectra of NR-20-H, NR-40-H, NR-60-H.
Table S1. Comparison of selected parameters of the whole pyrene-pyrazoquinoxaline NRs series.\textsuperscript{a,b}

| NR    | $\beta$ (nm) | $\rho$ (nm) | $\alpha$ (nm) | $\varepsilon (\rho)$ (M$^{-1}$cm$^{-1}$) | $\lambda_{em}$ (nm) | $\Phi^{c}$ | $E_{\text{GAP}}$ (eV)$^{b}$ | $E_{\text{LUMO}}$ (eV)$^{b}$ | $E_{\text{HOMO}}$ (eV)$^{i}$ |
|-------|--------------|--------------|---------------|------------------------------------------|--------------------|-----------|-----------------|-----------------|----------------|
| NR-10 | 378          | 528          | 604           | 185,527                                  | 622                | 0.27      | 1.97            | -3.60           | -5.57          |
| NR-20 | 385          | 544          | 605           | 426,294                                   | 623                | 0.14      | 1.96            | -3.63           | -5.60          |
| NR-20 | 383          | 545          | 604           | 425,358                                   | 623                | 0.18      | 1.97            | -3.62           | -5.59          |
| NR-30 | 387          | 549          | 605           | 730,137                                   | 623                | 0.11      | 1.96            | -3.69           | -5.66          |
| NR-40 | 385          | 550          | 604           | 789,164                                   | 623                | 0.16      | 1.97            | -3.72           | -5.69          |
| NR-60 | 387          | 553          | 604           | 1,198,074                                 | 625                | 0.11      | 1.97            | -3.74           | -5.71          |

\textsuperscript{a}The absorption and fluorescence ($\lambda_{ex} = 415$ nm) were measured in chloroform. \textsuperscript{b}The redox potentials (V vs Fc/Fc+) obtained by cyclic voltammetry in o-dichlorobenzene. The potentials are reported as $E_{1/2}=(E_{pa} + E_{pc})/2$, where $E_{pa}$ and $E_{pc}$ are the peak potentials in the anodic and the cathodic scans respectively. \textsuperscript{c}Fluorescence quantum yield was estimated using rhodamine 6G in EtOH (95%) as a reference. \textsuperscript{d}Optical band gap $E_{g}=hc/\lambda_{ae}≈1240/ \lambda_{ae}$ (nm); Where $\lambda_{ae}$ denotes the absorption edge wavelength in nm, obtained from offset wavelength derived from the lowest energy absorption band. \textsuperscript{e}The LUMO levels were estimated from the onset of the first reduction potential $E_{\text{LUMO}} = -(E_{\text{red}}^{\text{ONSET}} + 4.8$ eV). \textsuperscript{f}Estimated from $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{gap}}$. 


Table S2. Optical and Electronic Properties of NRs.\textsuperscript{a,b}

| NR   | β (nm) | ρ (nm) | α (nm) | ε (ρ) (M\textsuperscript{-1} cm\textsuperscript{-1}) | λ\textsubscript{em} (nm) | Φ\textsuperscript{c} | E\textsubscript{1/2\textsuperscript{I}} (V) | E\textsubscript{II} (V) | E\textsubscript{1/2\textsuperscript{III}} (V) | E\textsubscript{GAP} (eV) | E\textsubscript{LUMO} (eV) | E\textsubscript{HOMO} (eV) | Molar fluorescence brightness (M\textsuperscript{-1} cm\textsuperscript{-1})\textsuperscript{d} | Mass fluorescence brightness (g/L)\textsuperscript{1} cm\textsuperscript{-1})\textsuperscript{k} |
|------|--------|--------|--------|---------------------------------|-----------------|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|----------------|
| NR-20 | 383    | 545    | 604    | 425,358                         | 623             | 0.18   | -1.14          | -1.55\textsuperscript{d} | -1.76          | 1.97           | -3.62          | -5.59          | 5534           | 1.3            |
| NR-40 | 385    | 550    | 604    | 789,164                         | 623             | 0.16   | -1.16          | -1.56\textsuperscript{a} | -1.86          | 1.97           | -3.72          | -5.69          | 9950           | 1.3            |
| NR-60 | 387    | 553    | 604    | 1,198,074                       | 625             | 0.11   | -1.05          | -1.53\textsuperscript{f} | -1.73          | 1.97           | -3.74          | -5.71          | 8700           | 0.8            |

\textsuperscript{a}The absorption and fluorescence (λ\textsubscript{ex} = 415 nm) were measured in chloroform. \textsuperscript{b}The redox potentials (V vs Fc/Fc+) obtained by cyclic voltammetry in o-dichlorobenzene (Scan rate = 20 mV/s). The potentials are reported as $E_{1/2} = (E_{pa} + E_{pc})/2$, where $E_{pa}$ and $E_{pc}$ are the peak potentials in the anodic and the cathodic scans respectively. \textsuperscript{c}Fluorescence quantum yield was estimated using rhodamine 6G in EtOH (95%) as a reference. \textsuperscript{d}$E_{1/2}$. \textsuperscript{e}$E_{pc}$. \textsuperscript{f}$E_{pa}$. \textsuperscript{g}Optical band gap $E_g = \frac{hc}{\lambda_{ae}} \approx 1240/ \lambda_{ae}$ (nm); Where $\lambda_{ae}$ denotes the absorption edge wavelength in nm, obtained from offset wavelength derived from the lowest energy absorption band. \textsuperscript{h}The LUMO levels were estimated from the onset of the first reduction potential $E_{LUMO} = -(E_{red,ONSET} + 4.8$ eV). \textsuperscript{i}Estimated from $E_{HOMO} = E_{LUMO} - E_{gap}$. \textsuperscript{j}Molar fluorescence brightness = Φ·ε. \textsuperscript{k}Mass fluorescence brightness = (Φ·ε)/molecular weight.
Table S3. Frontier orbitals computed with the B3LYP Hamiltonian with the 6-31G(d,p) basis set in vacuum and with the 6-311+G(2d,2p) basis set in chloroform for all NRs. All geometries were optimized at the B3LYP-6-31G(d,p) level. The colour code is: LUMOs, HOMOs and gaps. All values in eV.

| NR  | 13  | 12  | 11  | 10  | 9   | 8   | 7   | 6   | 5   | 4   | 3   | 2   | 1   | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | Gap |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 20  | -1.2| -1.35| -1.61| -1.74| -1.74| -1.81| -1.86| -1.9| -3.22| -3.22| -3.28| -3.32| -3.59| -5.59| -5.66| -6 | -6.27| -6.27| -6.32| -6.55| -6.56| -6.58| -2.27|
| 40  | -1.87| -1.89| -1.91| -1.92| -1.96| -3.23| -3.23| -3.3| -3.31| -3.33| -3.35| -3.36| -3.6 | -5.6 | -5.67| -5.69| -5.69| 5.7 | -5.7 | -6.01| -6.03| -6.1 | -6.19| -2.24|
| 60  | -1.98| -3.23| -3.23| -3.3 | -3.31| -3.32| -3.33| -3.34| -3.35| -3.36| -3.37| -3.38| -3.6 | -5.6 | -5.67| -5.69| -5.69| 5.7 | -5.7 | -5.71| -5.71| -6.01| -2.22|
| Inf. | -3.38| -5.70 | | | | | | | | | | | | | | | | | | | | | -2.32|

B3LYP-6-31G(d,p)
### Table S4. TD-DFT non-zero transitions at the B3LYP-6-31G(d,p) level up.

**NR-20**

| Transition | eV  | nm  | Osc. Strength | Major contribs.                                      | Minor contribs.          |
|------------|-----|-----|---------------|------------------------------------------------------|--------------------------|
| 1          | 2.02 | 613 | 0.02          | H-1->L+1 (36%),HOMO->LUMO (61%)                     |                          |
| 3          | 2.07 | 598 | 0.07          | H-2->LUMO (93%)                                     | H-3->L+1 (3%)            |
| 4          | 2.08 | 595 | <0.005        | H-2->L+1 (60%),H-1->L+2 (18%),HOMO->L+3 (16%)      | H-3->LUMO (2%)           |
| 5          | 2.08 | 595 | 0.10          | H-1->L+3 (47%),HOMO->L+2 (49%)                      |                          |
| 6          | 2.08 | 595 | <0.005        | H-2->L+1 (30%),H-1->L+2 (31%),HOMO->L+3 (32%)      | H-3->LUMO (3%),H-2->L+3 (2%)|
| 8          | 2.11 | 587 | 0.02          | H-3->L+1 (92%)                                     | H-3->L+3 (3%),H-2->LUMO (3%)|
| 9          | 2.16 | 574 | <0.005        | H-3->L+3 (45%),H-2->L+2 (51%)                      |                          |
| 13         | 2.28 | 543 | 3.83          | H-5->L+1 (11%),H-4->LUMO (79%)                      | H-8->LUMO (2%),H-5->L+3 (3%)|

**NR-40**

| Transition | eV  | nm  | Osc. Strength | Major contribs.                                      | Minor contribs.          |
|------------|-----|-----|---------------|------------------------------------------------------|--------------------------|
| 1          | 2.02 | 615 | 0.01          | HOMO->L+1 (13%),HOMO->L+2 (21%),HOMO->L+3 (20%),HOMO->L+4 (24%),HOMO->L+5 (15%) | HOMO->LUMO (4%)         |
| 2          | 2.02 | 615 | 0.01          | H-1->L+1 (13%),H-1->L+2 (21%),H-1->L+3 (20%),H-1->L+4 (24%),H-1->L+5 (16%) | H-1->LUMO (4%)         |
| 3          | 2.06 | 601 | 0.14          | H-4->LUMO (18%),H-3->L+1 (27%),H-2->L+1 (12%)       | H-5->L+1 (6%),H-3->L+5 (3%),H-2->L+1 (2%),H-2->L+4 (3%) |
| 4          | 2.06 | 601 | <0.005        | H-3->LUMO (19%),H-3->L+2 (15%),H-2->L+1 (32%)       | H-5->LUMO (7%),H-4->L+1 (5%),H-3->L+1 (3%),H-3->L+4 (3%),H-2->L+5 (4%) |
| 5          | 2.07 | 600 | 0.03          | H-6->LUMO (10%),H-4->LUMO (45%)                     | H-6->L+2 (3%),H-5->L+1 (3%),H-5->L+3 (2%),H-4->L+2 (8%),H-3->L+1 (8%),H-2->L+2 (8%) |
| 8          | 2.08 | 596 | 0.02          | H-7->L+1 (10%),H-6->LUMO (29%),H-5->L+3 (15%),H-5->L+5 (10%),H-4->L+2 (19%) | H-6->L+2 (2%),H-4->L+4 (5%) |
| 9          | 2.08 | 595 | 0.01          | H-6->LUMO (32%),H-5->L+1 (34%),H-4->L+2 (16%)       | H-4->LUMO (3%),H-3->L+5 (3%),H-2->L+4 (2%) |
| Tr. | eV  | nm  | Osc. Strength | Major contribs.                                                                 | Minor contribs,            |
|-----|-----|-----|---------------|-----------------------------------------------------------------------------|----------------------------|
| 10  | 2.08| 595 | <0.005        | H-7->LUMO (14%),H-5->L+2 (16%),H-4->L+3 (23%),H-4->L+5 (15%)                | H-6->L+1 (5%),H-5->LUMO (7%),H-5->L+4 (2%),H-4->L+1 (4%),H-3->L+4 (2%) |
| 11  | 2.08| 595 | 0.05          | HOMO->L+6 (94%)                                                             |                            |
| 12  | 2.08| 595 | 0.07          | H-1->L+7 (94%)                                                              |                            |
| 13  | 2.08| 595 | <0.005        | H-3->L+4 (35%),H-2->L+3 (10%),H-2->L+5 (18%)                                | H-7->LUMO (3%),H-4->L+5 (2%),H-3->L+2 (7%),H-3->L+3 (5%),H-3->L+5 (8%) |
| 14  | 2.08| 595 | 0.03          | H-3->L+3 (11%),H-3->L+5 (17%),H-2->L+4 (35%)                                | H-2->L+2 (8%),H-2->L+3 (5%),H-2->L+5 (8%)                               |
| 16  | 2.11| 589 | <0.005        | H-7->L+1 (42%),H-6->L+2 (28%),H-5->L+3 (14%)                                | H-7->L+3 (5%),H-6->L+4 (4%)                                           |
| 18  | 2.12| 586 | 0.01          | H-7->L+3 (47%),H-7->L+5 (18%),H-6->L+2 (15%)                                | H-5->L+5 (5%),H-4->LUMO (5%),H-4->L+4 (4%)                              |
| 19  | 2.12| 585 | <0.005        | H-6->L+5 (22%),H-5->L+4 (33%),H-4->L+5 (12%)                                | H-7->L+4 (9%),H-6->L+3 (2%),H-5->L+2 (3%),H-4->L+3 (7%)                 |
| 20  | 2.12| 585 | 0.03          | H-7->L+5 (12%),H-6->L+4 (25%),H-5->L+3 (11%),H-5->L+5 (23%),H-4->L+4 (16%)  | H-4->L+2 (3%)                                                           |
| 23  | 2.17| 572 | 0.01          | H-3->L+6 (72%),H-2->L+6 (20%)                                               | H-5->L+6 (2%)                                                          |
| 24  | 2.17| 572 | <0.005        | H-3->L+7 (21%),H-2->L+7 (71%)                                               | H-5->L+7 (2%)                                                          |
| 33  | 2.23| 557 | 8.55          | H-10->LUMO (11%),H-9->L+1 (18%),H-8->LUMO (43%)                             | H-14->L+2 (3%),H-11->L+1 (8%),H-10->L+2 (5%),H-8->L+2 (3%)              |

**NR-60**

| Tr. | eV  | nm  | Osc. Strength | Major contribs.                                                                 |
|-----|-----|-----|---------------|-------------------------------------------------------------------------------|
| 1   | 2.02| 615 | <0.005        | H-1->L+5 (13%),H-1->L+9 (19%),HOMO->L+4 (12%),HOMO->L+6 (11%),HOMO->L+8 (20%)  |
| 2   | 2.02| 615 | 0.02          | H-1->L+4 (12%),H-1->L+6 (11%),H-1->L+8 (20%),HOMO->L+5 (13%),HOMO->L+9 (19%)   |
| 3   | 2.06| 601 | <0.005        | H-3->L+2 (19%),H-3->L+4 (12%),H-2->L+1 (11%),H-2->L+3 (19%)                   |
| 4   | 2.06| 601 | 0.15          | H-3->L+1 (11%),H-3->L+3 (19%),H-2->L+2 (19%),H-2->L+4 (12%)                   |
| 5   | 2.06| 601 | 0.17          | H-7->L+1 (11%),H-6->LUMO (43%)                                               | H-8->L+2 (5%),H-8->L+4 (3%),H-7->L+3 (5%),H-6->L+2 (6%),H-5->L+1 (5%),H-4->LUMO (9%) |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 6 | 2.07 | 600 | <0.005 | H-7→LUMO (19%), H-6→L+1 (12%), H-5→LUMO (10%), H-4→L+1 (17%) | H-8→L+1 (4%), H-7→L+4 (3%), H-6→L+3 (6%), H-5→L+2 (4%), H-5→L+4 (2%), H-3→L+4 (3%), H-2→L+4 (3%) |
| 7 | 2.07 | 599 | 0.01 | H-8→LUMO (13%), H-5→L+1 (17%), H-4→L+2 (14%) | H-9→L+1 (2%), H-7→L+1 (3%), H-6→LUMO (6%), H-6→L+2 (5%), H-6→L+4 (5%), H-5→L+5 (4%), H-4→LUMO (5%), H-4→L+4 (2%), H-3→L+3 (3%), H-3→L+5 (2%), H-2→L+4 (3%) |
| 9 | 2.08 | 597 | <0.005 | H-7→L+1 (13%) | H-10→L+2 (3%), H-10→L+4 (4%), H-9→L+1 (4%), H-9→L+3 (5%), H-9→L+7 (6%), H-8→LUMO (4%), H-8→L+2 (5%), H-8→L+4 (2%), H-8→L+6 (9%), H-7→L+1 (5%), H-7→L+3 (5%), H-7→L+5 (9%), H-6→L+2 (8%), H-6→L+4 (5%), H-5→L+3 (7%), H-4→L+2 (7%), H-4→L+4 (2%), H-4→L+6 (8%) |
| 12 | 2.08 | 596 | 0.01 | H-8→LUMO (10%), H-5→L+5 (12%), H-4→L+4 (13%) | H-11→L+3 (4%), H-10→LUMO (3%), H-10→L+2 (6%), H-9→L+1 (7%), H-7→L+7 (5%), H-6→L+6 (5%), H-5→L+3 (5%), H-5→L+9 (5%), H-4→L+6 (3%), H-4→L+8 (4%) |
| 14 | 2.08 | 596 | 0.02 | H-8→LUMO (10%), H-5→L+5 (12%), H-4→L+4 (13%) | H-11→L+1 (8%), H-8→LUMO (4%), H-7→L+1 (4%), H-7→L+3 (4%), H-7→L+7 (8%), H-6→L+4 (4%), H-6→L+6 (5%), H-5→L+3 (3%), H-5→L+5 (5%), H-5→L+7 (3%), H-5→L+9 (2%), H-4→L+2 (3%), H-4→L+4 (2%), H-4→L+6 (7%), H-4→L+8 (2%), H-3→L+9 (3%), H-2→L+8 (3%) |
| 16 | 2.08 | 595 | 0.01 | H-10→LUMO (14%) | H-10→LUMO (3%), H-5→L+9 (3%), H-4→L+8 (2%), H-3→L+5 (5%), H-3→L+7 (5%), H-2→L+4 (3%), H-2→L+6 (7%) |
| 17 | 2.08 | 595 | <0.005 | H-1→L+11 (47%), HOMO→L+10 (47%) | H-11→L+1 (5%), H-7→L+7 (7%), H-5→L+3 (3%), H-4→L+4 (3%) |
| 18 | 2.08 | 595 | 0.12 | H-1→L+10 (47%), HOMO→L+11 (47%) | H-11→L+1 (5%), H-7→L+7 (7%), H-5→L+3 (3%), H-4→L+4 (3%) |
| 20 | 2.08 | 595 | 0.02 | H-3→L+9 (27%), H-2→L+8 (28%) | H-10→LUMO (3%), H-5→L+9 (3%), H-4→L+8 (2%), H-3→L+5 (5%), H-3→L+7 (5%), H-2→L+4 (3%), H-2→L+6 (7%) |
| 22 | 2.09 | 594 | <0.005 | H-10→LUMO (26%), H-9→L+1 (23%), H-8→L+2 (15%) | H-11→L+1 (5%), H-7→L+3 (7%), H-5→L+3 (3%), H-4→L+4 (3%) |
| 26 | 2.11 | 588 | <0.005 | H-11→L+3 (15%), H-10→L+4 (10%) | H-11→L+3 (4%), H-11→L+7 (5%), H-10→L+2 (3%), H-10→L+4 (4%), H-10→L+6 (6%), H-9→L+3 (4%), H-9→L+5 (6%), H-9→L+7 (6%), H-8→L+2 (3%), H-8→L+4 (4%), H-8→L+6 (3%), H-8→L+8 (2%), H-7→L+3 (3%), H-7→L+5 (3%), H-7→L+7 (7%), H-7→L+9 (3%), H-6→L+4 (2%), H-6→L+6 (3%) |
| 28 | 2.11 | 586 | <0.005 | H-11→L+5 (17%), H-9→L+7 (13%) | H-11→L+3 (4%), H-11→L+7 (5%), H-10→L+2 (3%), H-10→L+4 (4%), H-10→L+6 (6%), H-10→L+8 (3%), H-9→L+5 (4%), H-9→L+9 (5%), H-8→L+6 (9%), H-8→L+8 (2%), H-7→L+5 (5%), H-5→L+9 (2%), H-4→L+8 (2%) |
|   |   |   |   |   |
|---|---|---|---|---|
| 29 | 2.12 | 586 | <0.005 | H-11->L+6 (16%), H-10->L+7 (21%), H-9->L+6 (13%) |
| 30 | 2.12 | 586 | 0.05 | H-11->L+7 (38%), H-10->L+6 (19%), H-9->L+5 (10%) |
| 31 | 2.12 | 585 | <0.005 | H-7->L+8 (11%), H-5->L+8 (21%), H-4->L+9 (19%) |
| 32 | 2.12 | 585 | 0.03 | H-8->L+8 (10%), H-7->L+9 (11%), H-5->L+9 (20%), H-4->L+8 (20%) |
| 34 | 2.14 | 580 | <0.005 | H-1->LUMO (10%), H-1->L+2 (24%), H-1->L+8 (11%), HOMO->L+1 (24%), HOMO->L+3 (12%), HOMO->L+9 (11%) |
| 36 | 2.17 | 572 | <0.005 | H-3->L+11 (45%), H-2->L+10 (45%) |
| 45 | 2.21 | 560 | 13.23 | H-15->L+1 (11%), H-14->LUMO (15%), H-13->L+1 (13%), H-12->LUMO (25%) |

H-11->L+4 (4%), H-10->L+3 (3%), H-10->L+5 (4%), H-10->L+9 (5%), H-9->L+8 (3%), H-8->L+5 (8%), H-7->L+4 (3%), H-5->L+8 (2%) 
H-11->L+5 (5%), H-11->L+9 (3%), H-10->L+4 (4%), H-9->L+3 (3%), H-8->L+4 (4%), H-6->LUMO (4%) 
H-10->L+9 (2%), H-9->L+8 (6%), H-8->L+9 (9%), H-6->L+9 (6%), H-5->L+6 (5%), H-4->L+5 (3%), H-4->L+7 (3%) 
H-10->L+8 (2%), H-9->L+9 (6%), H-6->L+8 (7%), H-5->L+5 (3%), H-5->L+7 (3%), H-4->L+6 (4%) 
H-1->LUMO (10%), H-1->L+2 (24%), H-1->L+8 (11%), HOMO->L+1 (24%), HOMO->L+3 (12%), HOMO->L+9 (11%) 
H-20->L+4 (2%), H-17->L+3 (4%), H-16->L+2 (7%), H-14->L+2 (4%), H-13->L+3 (2%), H-12->L+2 (3%)
MATERIALS AND METHODS

Reagents. All the commercial reagents utilized in the synthesis were used as received. Following compounds were synthesized as reported previously: 4,7-bis-[(triisobutylsilyl)ethynyl]benzo[c][1,2,5]thiadiazole-5,6-diamine 1,[1] 2,7-di-tert-butylpyrene-4,5,9,10-tetraone B[2] and compound A.[1]

Synthesis. All the reactions were performed in an oven-dried round-bottom flask, Schlenk tube or reaction vial. The required high temperature for the reactions was achieved by the use of an oil-bath or an aluminum heating block. The reaction progress was regularly monitored by thin-layer chromatography on TLC plates for which visualization was realized by visual observation under irradiation with UV lamp.

Purification. 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. Gel permeation chromatography was carried out using a Gehimadzu CBM-20A connected to a photodiode array detector Shimadzu SPD-M20A coupled with a Prominence LC-20AT HPLC and three polystyrene-packed columns coated with different pore size: 50, 500 and 1000 Å respectively.

Characterization. The NMR spectra were recorded with 400 or 500 MHz pulsed Fourier transform NMR spectrometer in deuterated solvents at room temperature. The chemical shift values are given in ppm and J values in Hz. Mass spectra were recorded by Dr. Estibaliz Gonzalez de San Roman Martinez on a Bruker Daltonics-Autoflex MALDI-TOF mass spectrometer using DCTB or DCTB+Ag⁺ as matrix. High-resolution mass spectra were recorded by Dr. Javier Calvo on a UltrafleXtreme III MALDI tandem mass spectrometer (Bruker) using DCTB or DCTB+Ag⁺ as matrix.

Absorption and emission spectroscopy. The absorption spectra were recorded with a double beam UV/VIS/NIR spectrophotometer (PerkinElmer – Lambda 950) and the emission spectra were collected on a fluorescence spectrometer (PerkinElmer – LS 55) in CHCl₃ in both cases.

The molar absorptivity values (ε) were estimated from the maximum values of the ρ band. For this, several measurements were made at different concentrations.
Figure S7. Molar absorptivity values of a) NR-20, b) NR-40 and c) NR-60.

Fluorescence quantum yields were determined by the comparative method using Rhodamine 6G (Φf = 0.95 in ethanol) as a standard. Quantum yields Φ were calculated following the next equation:

\[
\Phi = \Phi_r \left( \frac{n_s}{n_r} \right) \left( \frac{m_s}{m_r} \right)^2
\]

Where: Φ for fluorescence quantum yield, \( m \) for gradient of the plot of integrated fluorescence intensity against absorbance, \( n \) for refractive index of the solvent. \( r \) and \( s \) subscripts refer to the reference and unknown.
**Cyclic voltammetry.** Electrochemical behavior of the compounds was studied using cyclic voltammetry in a three-electrode single-compartment cell consisting of a glassy carbon working electrode, silver wire as the reference electrode, and a platinum wire as the counter electrode with ferrocene (Fc) as an internal reference. The cell was connected to the computer controlled potentiostat (Princeton Applied Research - PARSTAT 2273). The measurements were carried out under N$_2$ atmosphere in anhydrous o-dichlorobenzene using tetrabutylammonium hexafluorophosphate (0.05 M) as the supporting electrolyte. The potentials of all the reversible peaks are reported as $E_{1/2} = (E_{pa} + E_{pc})/2$ in V vs Fc/Fc$^+$ couple.

**Calculations.** To calculate the 3D structure of the NRs, semiempirical quantum mechanics were used to explore different conformers of the simplified NR-H molecules with GFN-xTB Hamiltonians which allow computing efficiently systems with thousands of atoms.$^3$ To predict the most stable 3D structure of the different NRs, a simulated annealing run with the GFN0 method was first performed followed by ranking by, the more accurate, GFN2 method.$^4$ In addition, a global conformation search based on metadynamics with the CREST methodology and the GFNFF, GFN0 and GFN2 Hamiltonians$^5$ was performed for NR-20-H. The different so-produced conformers were finally ranked with DFT at the B3LYP-6-31G(d,p) level which confirmed the identity of the global minima which was then built for NR-40-H and NR-60-H. TD-DFT calculations were performed on the lowest energy minimum found with the B3LYP-6-311+G(d,p)-Chloroform/B3LYP-6-31G(d,p) Hamiltonian. NICS(0) and ACID plots were computed with B3LYP-6-31G(d,p) for NR-20-H, NR-40-H, NR-60-H. The NICS and the BLA (Bond Length Alternation) patterns were graphically analyzed with the help of the open-source software Jmol.$^6$ All the DFT calculations were performed with the program Gaussian09.$^7$
Synthesis of C

Compound B (625 mg, 1.67 mmol) was suspended in acetic acid (80 mL) and the mixture was heated till 80 ºC. Diamine 1 (340 mg, 0.56 mmol) was dissolved in dichloromethane (10 mL) added dropwise (1 mL/h) and the reaction was stirred at 80ºC for one day. The reaction was quenched with NaHCO₃ (aq.) and the product was extracted with dichloromethane. Organic phase was washed with brine, dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The solid was loaded onto a chromatographic column (dichloromethane: hexane 1:1). The product was isolated as a dark-red solid (352 mg, 66%). ¹H NMR (400 MHz, Chloroform-d) δ 9.74 (d, J = 2.1 Hz, 2H), 8.65 (d, J = 2.1 Hz, 2H), 2.10 (dp, J = 13.3, 6.6 Hz, 6H), 1.60 (s, 18H), 1.11 (d, J = 6.6 Hz, 36H), 0.96 (d, J = 6.9 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 179.88, 155.11, 152.98, 143.75, 141.20, 131.19, 130.98, 130.20, 130.10, 129.53, 114.55, 114.55, 113.69, 101.24, 35.58, 31.31, 26.51, 25.16, 25.06. HRMS (MALDI, pos.) (m/z): [M]⁺ calcd. for C₅₈H₇₆N₄O₂SSi₂, 948.5226; found 948.5241.

Synthesis of D

Compound A (138 mg, 0.14 mmol) and compound C (100 mg, 0.11 mmol) were dissolved in cloroform (3 mL) and acetic acid (1 mL). The mixture was stirred two days at 110 ºC. The reaction was quenched with NaHCO₃ (aq.) and the product was extracted with dichloromethane. Organic phase was washed with brine, dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The solid was
loaded onto a chromatographic column (dichloromethane: hexane 1:1). The product was isolated as a dark-red solid (194 mg, 96%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.97 (d, $J = 2.1$ Hz, 2H), 9.91 (d, $J = 2.1$ Hz, 2H), 9.56 (d, $J = 2.0$ Hz, 2H), 8.22 (d, $J = 2.0$ Hz, 2H), 4.39 (s, 4H), 3.87 (s, 4H), 2.14 (ddt, $J = 15.3$, 13.3, 6.7 Hz, 12H), 1.84 (s, 18H), 1.65 (s, 18H), 1.15 (d, $J = 6.6$ Hz, 36H), 1.12 – 1.10 (m, 36H), 1.02 (d, $J = 6.9$ Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.99, 151.82, 151.40, 145.39, 144.45, 142.07, 141.99, 141.63, 132.39, 129.70, 129.26, 127.49, 127.36, 127.18, 127.10, 126.29, 124.70, 124.83, 114.23, 112.85, 112.56, 102.39, 101.53, 93.42, 88.83, 61.89, 35.87, 35.53, 32.15, 31.77, 26.57, 26.50, 25.26, 25.21, 25.16. HRMS (MALDI, pos.) (m/z): [M]$^+$ calcd. for C$_{120}$H$_{160}$N$_8$O$_4$Si$_4$, 1921.1357; found 1921.1483.

**Synthesis of AA**

![Chemical structure](image)

Compound D (200 mg, 0.1 mmol) was dissolved in dry diethyl ether (8 mL) and cold down to 0°C. LiAlH$_4$ (80 mg, 20 eq) was added portionwise and the reaction was stirred overnight at room temperature. The reaction was quenched with NH$_4$Cl (aq.) and the product was extracted with dichloromethane. Organic phase was washed with brine, dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The solid was loaded onto a chromatographic column (dichloromethane: hexane 1:1). The product was isolated as a brown solid (189 mg, quantitative). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.92 (d, $J = 6.5$ Hz, 4H), 9.59 – 9.55 (m, 2H), 8.24 – 8.19 (m, 2H), 4.86 (s, 3H), 4.39 (s, 4H), 3.88 (s, 4H), 2.10 (ddq, $J = 19.9$, 13.3, 6.6 Hz, 12H), 1.83 (s, 18H), 1.65 (s, 18H), 1.12 (t, $J = 6.9$ Hz, 84H), 0.97 (d, $J = 6.9$ Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.75, 150.46, 145.23, 144.35, 142.11, 141.94, 132.32, 129.76, 129.19, 127.02, 126.13, 125.98, 125.30, 124.67, 121.66, 112.16, 102.50, 93.45, 61.80, 35.85, 35.52, 32.30, 31.78, 26.55, 26.50, 25.30, 25.25. HRMS (MALDI, pos.) (m/z): [M]$^+$ calcd. for C$_{120}$H$_{164}$N$_8$O$_4$Si$_4$, 1894.2027; found 1894.2003.
Synthesis of NR-20

Compound AA (40 mg, 0.021 mmol) and compound B (3 mg, 0.008 mmol) were dissolved in chloroform (3 mL) and acetic acid (1 mL). The mixture was refluxed for two days. The reaction was quenched with NaHCO$_3$ (aq.) and the product was extracted with chloroform. Organic phase was washed with brine, dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The solid was loaded onto a chromatographic column (dichloromethane: hexane 1:1). The product was precipitated in methanol and isolated as a bright purple solid (22 mg, 67%). $^1$H NMR (400 MHz, Chloroform-$d$) δ 10.04 (d, $J = 8.4$ Hz, 12H), 9.58 (d, $J = 1.5$ Hz, 4H), 8.23 (d, $J = 1.6$ Hz, 4H), 4.39 (s, 8H), 3.88 (s, 8H), 2.22 – 2.13 (m, 24H), 1.91 (s, 54H), 1.66 (s, 36H), 1.15 (dd, $J = 14.8$, 6.5 Hz, 192H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.99, 151.46, 144.93, 144.72, 142.44, 142.23, 132.55, 129.87, 129.80, 129.74, 127.50, 127.26, 126.44, 124.88, 122.00, 112.69, 102.60, 93.60, 62.05, 36.13, 35.70, 32.51, 31.95, 26.71, 26.69, 25.49, 25.45, 25.36, 25.32. MS (MALDI-TOF) (m/z): [M+Ag]$^+$ calcd. for C$_{264}$H$_{342}$AgN$_{16}$O$_8$Si$_8$, 4200.292; found 4199.445.

Synthesis of NR-40

NR-20 (20 mg, 4.9 µmol) was dissolved in TFA and water was added. The reaction was stirred at room temperature two days. Aqueous work-up was carried out and the product was extracted with chloroform, dried over sodium sulfate, filtrated and solvent was eliminated by rotary evaporation. The purple solid was used in next step without further purification. The solid obtained was dissolved in chloroform (3 mL) and acetic acid (1 mL) and compound AA (23 mg, 12 µmol) was added. The mixture was refluxed for two days. The crude was extracted with chloroform and aqueous work-up was carried out. The organic phase was dried
over sodium sulfate, filtrated and solvent was eliminated by rotary evaporation. The solid was purified by GPC in chloroform (flow rate = 3 mL/min, retention time = 85 min) and reprecipitated in methanol. The product was isolated as a dark purple solid (8 mg, 22 % for the last two steps). 

\[ ^1\text{H NMR (500 MHz, Chloroform-}\text{d}) \delta 10.14 – 9.99 (m, 28H), 9.58 (d, J = 1.6 Hz, 4H), 8.23 (d, J = 1.6 Hz, 4H), 4.39 (s, 8H), 3.88 (s, 8H), 2.20 (ddt, J = 24.1, 13.2, 6.5 Hz, 48H), 1.92 (d, J = 13.0 Hz, 126H), 1.66 (s, 36H), 1.19 (dt, J = 11.3, 5.7 Hz, 288H), 1.14 – 1.12 (m, 96H). \]

\[ ^13\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 151.85, 151.40, 151.34, 144.81, 144.62, 144.59, 142.31, 142.09, 132.43, 129.83, 129.72, 129.66, 127.41, 127.36, 127.27, 127.12, 126.29, 124.72, 121.97, 121.85, 112.79, 112.53, 102.47, 93.45, 61.78, 36.00, 35.55, 32.38, 32.36, 31.79, 29.69, 26.57, 26.52, 25.34, 25.29, 25.23, 25.19. \]

\[ \text{MS (MALDI-TOF) (m/z): [M+Ag]^{+} \text{ calcd. for: C}_{496}\text{H}_{646}\text{AgN}_{32}\text{O}_{8}\text{Si}_{16}, 7742.068; found 7742.256} \]

**Synthesis of NR-60**

NR-40 (14 mg, 1.8 µmol) was dissolved in TFA and water was added. The reaction was stirred at room temperature two days. Aqueous work-up was carried out and the product was extracted with chloroform, dried over sodium sulfate, filtrated and solvent was eliminated by rotary evaporation. The purple solid was used in next step without further purification. The solid obtained was dissolved in chloroform (3 mL) and acetic acid (1 mL) and compound AA (17 mg, 9 µmol) was added. The mixture was refluxed for two days. The crude was extracted with chloroform and aqueous work-up was carried out. The organic phase was dried over sodium sulfate, filtrated and solvent was eliminated by rotary evaporation. The solid was purified by GPC in chloroform (flow rate = 3 mL/min, retention time = 75 min) and reprecipitated in methanol. The product was isolated as a dark purple solid (5 mg, 26 % for the last two steps). 

\[ ^1\text{H NMR (500 MHz, Chloroform-}\text{d}) \delta 10.05 (d, J = 15.0 Hz, 45H), 9.58 (s, 4H), 8.23 (s, 4H), 4.39 (s, 8H), 3.87 (s, 8H), 2.29 – 2.14 (m, 78H), 1.92 (d, J = 13.2 Hz, 196H), 1.66 (s, 37H), 1.18 – 1.12 (m, 281H). \]

\[ ^13\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 151.86, 151.40, 144.82, 144.63, 142.33, 142.11, 132.44, 129.68, 127.38, 127.14, 126.30, 124.70, 121.99, 121.87, 112.81, 112.57, 102.47, 93.46, 61.64, 37.46, 37.12, 36.03, 32.40, 32.10, 31.94, 31.81, 29.72, 26.58, 25.35, 25.25. \]

\[ \text{MS (m/z): While the structure has been confirmed unambiguously by NMR, we have not been able to detect the molecular ion peak. Similar observations have been reported for another type of high molecular weight pyrene NRs.}^{[8]} \]
**$^1$H NMR and $^{13}$C NMR SPECTRA**

$^1$H NMR of compound C in CDCl$_3$

$^{13}$C NMR of compound C in CDCl$_3$
1H NMR of compound D in CDCl₃

13C NMR of compound D in CDCl₃
$^{1}H$ NMR of compound AA in CDCl$_3$

$^{13}C$ NMR of compound AA in CDCl$_3$
\textbf{H NMR of compound NR-20} in CDCl$_3$

\textbf{\textsuperscript{13}C NMR of compound NR-20} in CDCl$_3$
$^1$H NMR of compound NR-40 in CDCl$_3$

$^{13}$C NMR of compound NR-40 in CDCl$_3$
$^1$H NMR of compound NR-60 in CDCl$_3$

$^{13}$C NMR of compound NR-60 in CDCl$_3$
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