Supporting Information

Convergent Synthesis of 10 nm Aryleneethynylene Molecular Wires by an Iterative Regioselective Deprotection/Sonogashira Coupling Protocol

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Discussion of the Optical Properties of the Compounds in Table 1.

If the wavelength of the absorption / emission is converted into energy and plotted against the inverse number of \( \pi \)-units \( (1/n, \text{where each phenyl ring or triple bond is counted as one } \pi\)-unit) straight lines are obtained (Figure S1). A general equation for the straight lines is:

\[
\Delta E = an + b \quad (1)
\]

where \( \Delta E \) is the absorption / emission energy, \( N \) is the inverse number of \( \pi \)-units, namely, \( 1/n \), \( a \) is the slope of the line (found to be 1.91 for the absorption, and 1.69 for the photoluminescence) and \( b \) is the intersection of the line with the vertical energy axis (found to be 3.03 eV for the absorption and 2.72 eV for the photoluminescence).

As we know that

\[
\Delta E (\text{eV}) = \frac{h \nu}{\lambda} = \frac{1240}{\lambda} \quad (2)
\]

where \( h \) is Plank’s constant, \( \nu \) is the frequency of the absorption / emission, \( c \) is light velocity, equation (1) can be translated as:

\[
\frac{1240}{\lambda} = an + b \quad (3)
\]

Thus,

\[
\lambda = \frac{1240}{an + b} \quad (4)
\]

Figure S2 shows a plot of absorption / emission wavelengths against \( n \), with \( n \) extrapolated up to 1000. Thus the straight lines in Figure S1 and the curves in Figure 5 are different mathematical representations of the same experimental result. Therefore, whichever equation is plotted the same
conclusion should be obtained, which is that the slopes of the lines change significantly at some value of \( n < 50 \) (Figure S2).

To describe the lines in Figure 5 of the text, the equation (5) of red-shift (\( RS \)) as a function of \( n \) can also be derived:

\[
\Delta \lambda = \lambda_{n+1} - \lambda_n \\
= \frac{1240(n+1)}{a+b(n+1)} - \frac{1240n}{a+bn} \\
= \frac{1240(n+1)(a+bn) - 1240n[a+b(n+1)]}{[a+b(n+1)][a+bn]} \\
= \frac{1240a}{a^2 + ab + 2abn + b'nn'}
\]  

\( (5) \)

Where \( \Delta \lambda \) is the value of a \( RS \) caused by a single increment of the \( \pi \)-unit. The percentage form of this \( RS \) is:

\[
RS\% = \frac{\Delta \lambda}{\lambda_0} \times 100 = \frac{124000a}{(a^2 + ab + 2abn + b'nn')\lambda_0}
\]  

\( (6) \)

Where \( \lambda_0 \) is the absorption / emission wavelength of the shortest molecule of the series, namely 340 / 380 nm for compound 4.

Based on equation (6), if we plot \( RS\% \) against the number of \( \pi \)-units (\( n \)) (Figure S3), it can be seen that as the molecules get longer, the red-shift gets progressively smaller. The \( RS \) value will approach zero as \( n \) approaches infinity. However, similar to Figure S2, a turning point also exists in this \( RS \) plot. This shows that short and long molecules red-shift following two different trends (red line in Figure S2). We propose that the converging point of the two approximately straight lines (\( S \), Figure S2) is the theoretical saturation point. If we set an \( RS\% \) value as threshold, the saturation number of \( \pi \)-units can be calculated, e.g., at 5% \( n \approx 6 \), at 2% \( n \approx 10 \), at 1% \( n \approx 15 \) and at 0.1% \( n \approx 50 \).

The red-shift values can also be converted into energies (\( E_{RS} = \frac{-a}{n(n+1)} \) eV). The plot of \( E_{RS} \) values of absorption against \( n \) is given in Figure S4. From Figure S4 the same saturation conclusion can be drawn, although a straight line can also be obtained by plotting \( E_{RS} \) as a function of the inverse number of \( n(n+1) \) which has no physical meaning.

As a conclusion, the conjugation length of conjugated oligomers/polymers is proven to be limited by extrapolating the absorption/emission data as a function of the number of the \( \pi \)-units. The red-shifts caused by a progressive increase in the number of \( \pi \)-units within this length follow a different trend from those incurred beyond this length. For the structures reported in this paper, the saturation length is estimated to be between 15 and 20 \( \pi \)-units.
FIGURE S1. The energy of absorption (upper) and emission (lower) plotted against the inverse number of π-units for compounds 4, 6, 8, 10, 12, 14, 16 and 17 (where each phenyl ring or triple bond is counted as one π-unit).

FIGURE S2. A plot of absorption/emission wavelengths against $n$, with $n$ extrapolated up to 1000.

FIGURE S3. The percentage absorption red-shift ($RS\%$) plotted against the number of π-units, $n$. 
FIGURE S4. A plot of the absorption red-shift energy ($E_{RS}$) against $n$. 