Supporting Information

Photophysics of Threaded sp-Carbon Chains: The Polyne is a Sink for Singlet and Triplet Excitation

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**Figure S2.** Excited state dynamic changes in dumbbell $H$ on excitation at 266 nm in TRIR spectra. (a) Single exponential decay of 1613 cm$^{-1}$ band in deoxygenated ($\tau_2 = 16.0 \pm 3.6$ µs) and (b) air-saturated ($\tau_1 = 1.2 \pm 0.1$ µs) CH$_2$Cl$_2$ (laser energy = 200 nJ). This enhanced decay in the presence of oxygen supports assignment of the 1613 cm$^{-1}$ band to the triplet excited state of the hexayne.

**Figure S3.** (a) Shift in the TRIR peak of hexayne dumbbell $H$ at 2055–2077 cm$^{-1}$ at 0–15 ps after excitation. (b) TRIR spectra of $H$ in fingerprint region at early time delays (0–3 ps). Excitation $\lambda = 310$ nm; laser energy = 200 nJ; solvent: CH$_2$Cl$_2$.

**Figure S4.** TA spectra and excited state kinetics of hexayne dumbbell $H$ (a,b, laser energy = 50 nJ), rotaxane $H\subset M$ (c,d, laser energy = 70 nJ) and $H\subset M(Re)$ (e,f, laser energy = 70 nJ); excited at 310 nm; solvent: CH$_2$Cl$_2$. 

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**Figure S5.** Transient absorption spectra of hexayne H in NIR region following excitation at 310 nm. (a) The decay of \( S_n \) state and (b) its single exponential kinetics (1085 nm, \( \tau_1 = 0.82 \pm 0.13 \) ps). Excitation \( \lambda = 310 \) nm; laser energy = 60 nJ, solvent: CH\(_2\)Cl\(_2\).

**Figure S6.** Single exponential decay of 1504 cm\(^{-1}\) TRIR band (\( \tau_1 = 2.07 \pm 0.24 \) ns) of the macrocycle M on excitation at 350 nm. Laser energy = 100 nJ; solvent: CH\(_2\)Cl\(_2\).

**Figure S7.** (a) Excited state TA spectra of macrocycle M on excitation at 350 nm; laser energy = 100 nJ; solvent: CH\(_2\)Cl\(_2\). (b) The kinetics of the 365 nm band assigned to the decay of the singlet state (\( \tau_1 = 1.8 \pm 0.15 \) ns), while the growth of the band at 436 nm is assigned to the triplet state formation and has similar kinetics (\( \tau_1 = 3.2 \pm 0.8 \) ns).
Figure S8. Excited state dynamics in rotaxane HCM on excitation at 310 nm from TRIR spectra. (a) Early-time spectral changes in the fingerprint region. (b) Biexponential growth of 1741 cm\(^{-1}\) singlet hexayne band \((\tau_1 = 4.3 \pm 1.6\) ps, \(A_1 = 0.43; \tau_2 = 0.19 \pm 0.02\) ps, \(A_2 = 0.57)\). At early time delays, the growth of the singlet S\(_1\) hexayne at 1741 cm\(^{-1}\) is biexponential, in contrast to the single-exponential growth of the same band in free dumbbell H (Figure 3c). This behavior results from two processes operating in parallel: (a) excitation of the macrocycle and energy transfer to the polyyne \((\tau_1)\), and (b) direct excitation of the hexayne \((\tau_2 < 200\) fs; instrument response limited). Partial direct excitation of the macrocycle is confirmed by the band at 1500–1600 cm\(^{-1}\) (Figure S8a), which decays over 4 ps due to energy transfer to the hexayne dumbbell.

Figure S9. (a) Excited state dynamic changes in rotaxane HCM on excitation with ns laser at 266 nm in TRIR spectra. Single exponential decay of 2047 cm\(^{-1}\) band of triplet dumbbell \((\tau_1 = 0.95 \pm 0.04\) µs), single exponential recovery of 2189 cm\(^{-1}\) \(\nu(\text{C}=\text{C})\) bleach \((\tau_1 = 0.90 \pm 0.03\) µs) and single exponential decay of the 1610 cm\(^{-1}\) band \((\tau_1 = 1.04 \pm 0.05\) µs) in air-saturated CH\(_2\)Cl\(_2\). (b) The kinetics of decay of the dumbbell triplet state in rotaxane HCM in deoxygenated CH\(_2\)Cl\(_2\) \((\tau_1 = 14.0 \pm 2.2\) µs).
Figure S10. Excited state dynamic changes of rotaxane H⊂M on excitation at 310 nm in TA spectra. (a) Single exponential growth of the band at 422 nm and (b) its kinetics ($\tau_1 = 1.8 \pm 0.2$ ps).

Figure S11. TA spectra measured in deoxygenated CH$_2$Cl$_2$ upon the excitation of rotaxane H⊂M with 355 nm laser in presence of β-carotene. After 1 ps the singlet polyyne band at 422 nm is visible, later, 1 ns after excitation, the singlet polyyne band disappears and new band appear at 526 nm corresponding to the triplet excited state β-carotene (Gust, D.; Moore, T. A.; Moore, A. L.; Devadoss, C.; Liddell, P. A.; Hermant, R.; Nieman, R. A.; Demanche, L. J.; DeGraziano, J. M.; Gouni, I. J. Am. Chem. Soc. 1992, 114, 3590–3603). The triplet β-carotene formation is the result of the energy transfer from triplet excited polyyne. Unfortunately, the triplet polyyne band at 343 nm is obscured by excitation laser and is not visible.

Figure S12. The kinetics of the decay of triplet excited M(Re) in deoxygenated CH$_2$Cl$_2$, extracted from the bleach recovery of $A''$ ground state band (2022 cm$^{-1}$, $\tau_1 = 92.3 \pm 6.4$ ns) and the decay of excited state $A''$ band (2051 cm$^{-1}$, $\tau_1 = 93.6 \pm 7.2$ ns).
Figure S13. TRIR spectra of the M(Re) and the kinetics of the bands excited at 350 nm (a–d, laser energy = 200 nJ), H⊂M(Re) and its kinetics excited at (e–h) 350 nm (laser energy = 100 nJ) and (i–l) excited at 310 nm; laser energy = 100 nJ; solvent: CH₂Cl₂.
**Figure S14.** TRIR spectra of Re(CO)$_3$Cl-rotaxane complex HCM(Re) in polyyne stretching region at early time delays (0–15 ps). Excitation $\lambda = 350$ nm; laser energy = 200 nJ, solvent: CH$_2$Cl$_2$.

**Figure S15.** Comparison of IR and TRIR spectral intensities for HCM(Re). To estimate the triplet energy transfer efficiency, we compared the relative intensities of the C=C and A'(1) C=O bands in the ground state IR spectrum ($A/B = GS_r = 6.71$; top) with that of the same bands when maximally bleached (15 ps and 45 ns after excitation, respectively, under air) in the TRIR spectra ($C/D = ES_r = 6.81$). The triplet energy transfer efficiency ($^3\text{EET}$) was estimated using the equation:

$$\Phi_{^3\text{EET}} = \frac{GS_r}{ES_r}$$

This calculation gave $\Phi_{^3\text{EET}} = 6.71/6.81 = 0.99$. The same calculation was also carried out using TRIR spectra from an oxygen-free solution of HCM(Re); under these conditions, the bleach of the C=C and A'(1) C=O bands were most intense 15 ps and 5.50 $\mu$s after excitation, respectively; $C/D = ES_r = 6.72$; $\Phi_{^3\text{EET}} = 6.71/6.72 = 1.00$. 
Figure S16. TRIR spectra of HCM(Re) showing the mutual electronic perturbation of components. Top picture shows the enhanced ground state $\nu$(C≡C) band absorption (circled) due to nearby triplet M(Re). Bottom picture shows that despite the transients of M(Re) disappeared due to EET, however, the ground state $\nu$(CO) bands (negative bleach) still are visible as an effect of nearby triplet dumbbell.

Figure S17. (a) TRIR spectra of Re(CO)$_3$Cl-rotaxane HCM(Re) complex in fingerprint region. (b) Kinetics of 1610 cm$^{-1}$ triplet band in oxygen containing ($\tau_1 = 0.81 \pm 0.02$ µs) and (c) deoxygenated CH$_2$Cl$_2$ ($\tau_1 = 20.2 \pm 1.7$ µs). Excitation $\lambda = 266$ nm; laser energy = 100 nJ.

Figure S18. TA spectra of Re(CO)$_3$Cl-rotaxane HCM(Re) in CH$_2$Cl$_2$ (excitation $\lambda = 310$ nm). (a) The growth of the singlet and triplet polyyne transient bands, and (b) the single exponential growth of singlet $S_1$ polyyne transient at 422 nm ($\tau_1 = 0.60 \pm 0.6$ ps).
Figure S19. Comparison of calculated ((TD-/U)B3LYP/cc-pVTZ) vibrational mode bond length changes (bars) and the absolute deviation of the equilibrium bond length from the mean bond length in each (S₀, S₁, T₁) state (red lines). The figure shows that higher (lower) energy vibrations (left (right) plots) involve bonds with a greater (lesser) length deviation from the mean – i.e. more alternate (cumulenic) character. Reported frequencies are scaled by a factor of 0.96. Only the CC bonds in the hexayne C₁₂ fragment are reported – the H₃C-C bonds are omitted.
Table S1. Excited state bands, transitions and lifetimes of Re(CO)$_3$Cl-rotaxane H⊂M(Re) excited at 310 nm in CH$_2$Cl$_2$.

| TRIR band | Lifetime (τ) | Assignment | TA band | Lifetime (τ) | Assignment |
|-----------|--------------|------------|---------|--------------|------------|
| 1892 cm$^{-1}$ | 10.8 ± 2.0 ps, $A_1 = 0.38$, 1.14 ± 0.11 ns, $A_2 = 0.62$ | T$_1$, νCO | 422 nm | 0.60 ± 0.6 ps | S$_1$ growth |
| 1930 cm$^{-1}$ | 8.20 ± 0.88 ps, $A_1 = 0.5$, 1.60 ± 0.17 ns, $A_2 = 0.5$ | T$_1$, νCO | 422 nm | 0.34 ± 0.01 ns | S$_1$ decay |
| 2023 cm$^{-1}$ | 9.60 ± 1.15 ps, $A_1 = 0.43$, 1.71 ± 0.19 ns, $A_2 = 0.57$ | T$_1$, νCO | 1610 cm$^{-1}$ | 12.2 ± 1.6 ps, $A_1 = 0.35$, 0.54 ± 0.04 ns, $A_2 = 0.65$ | T$_1$ growth of hexayne |
| 2075 cm$^{-1}$ | 0.36 ± 0.03 ps | S$_1$ decay of hexayne |
| 1741 cm$^{-1}$ | 0.35 ± 0.01 ns | S$_1$ decay of hexayne |

Further details of (TD-)DFT calculations

Calculations started from a linear methyl-capped hexayne (D$_3$ symmetry), which was subject to geometry optimization followed by frequency calculation. As mentioned in the main text, the RI-J approximation (multipole accelerated resolution of the identity) was used. The absence of imaginary frequencies confirmed that a minimum had been reached. The excited state geometry was obtained by a TD-DFT geometry optimization of the lowest energy root, taking the optimized ground state structure as a starting point. The RI-J approximation was not used in TD-DFT calculations. The vibrational frequencies of the S$_1$ excited state were obtained by calculating force constants within the framework of TD-DFT.

The T$_1$ state was tackled by taking the optimized geometry of the S$_0$ step and applying C$_2$ symmetry and a triplet-occupation Hückel wavefunction guess. The resulting system was subject to geometry optimization (UB3LYP or UPBE0) followed by frequency calculation. These calculations were able to take advantage of the RI-J approximation.

Test calculations on a helical/S-shaped polyyne and a U-shaped polyyne converged to local minima – not to linear structures. However, these local minima had higher energies than the linear structures. Vibrational frequency trends were invariant of polyyne conformation (linear, bent, S-shaped).

Calculated vibrational frequencies, reduced masses, IR intensities and mode symmetries are reproduced below for S$_0$, S$_1$ and T$_1$ at the B3LYP/cc-pVTZ level of theory, within the frequency range 1700–2350 cm$^{-1}$. The frequencies are uncorrected (a scaling factor of 0.96 is generally recommended).
Table S2. Calculated (B3LYP/cc-pVTZ) vibrational properties for the singlet ground state (S\textsubscript{0}) of H\textsubscript{3}C-C\textsubscript{12}-CH\textsubscript{3}. Frequencies are reported uncorrected, and only vibrations in the range 1700–2350 cm\textsuperscript{-1} are reported.

| mode | 49    | 50    | 51    | 52    | 53    | 54    |
|------|-------|-------|-------|-------|-------|-------|
| frequency | 2128.37 | 2147.67 | 2214.4 | 2262.03 | 2299.02 | 2315.43 |
| symmetry | a2     | a1    | a1    | a2    | a2    | a1    |
| IR active? | YES    | NO    | NO    | YES   | YES   | NO    |
| |dDIP/dQ| (a.u.) | 0.0006 | 0       | 0.0068 | 0.012  | 0      |
| intensity (km/mol) | 0.72    | 0     | 0     | 81.28  | 257.14 | 0      |
| intensity (%) | 0.28    | 0     | 0     | 31.61  | 100    | 0      |
| Raman active? | NO    | YES   | YES   | NO    | NO    | YES   |
| reduced mass (g/mol) | 11.985  | 11.997 | 11.963 | 12.004 | 11.896 | 11.919 |

Table S3. Calculated (TD-B3LYP/cc-pVTZ) vibrational properties for the first singlet excited state (S\textsubscript{1}) of H\textsubscript{3}C-C\textsubscript{12}-CH\textsubscript{3}. Frequencies are reported uncorrected, and only vibrations in the range 1700–2350 cm\textsuperscript{-1} are reported.

| mode | 49    | 50    | 51    | 52    | 53    | 54    |
|------|-------|-------|-------|-------|-------|-------|
| frequency | 1860.44 | 1936.8 | 2027.6 | 2084.51 | 2182.74 | 2191.96 |
| symmetry | a2     | a2    | a1    | a1    | a1    | a2    |
| IR active? | YES    | YES   | NO    | NO    | NO    | YES   |
| |dDIP/dQ| (a.u.) | 0.0121 | 0.0006 | 0      | 0      | 0.0102 |
| intensity (km/mol) | 258.13  | 0.63  | 0     | 0      | 0      | 185.55 |
| intensity (%) | 100    | 0.24  | 0     | 0      | 0      | 71.88  |
| Raman active? | NO    | NO    | YES   | YES   | YES   | NO    |
| reduced mass (g/mol) | 11.82  | 11.973 | 11.997 | 12     | 11.79  | 11.845 |

Table S4. Calculated (UB3LYP/cc-pVTZ) vibrational properties for the first triplet excited state (T\textsubscript{1}) of H\textsubscript{3}C-C\textsubscript{12}-CH\textsubscript{3}. Frequencies are reported uncorrected, and only vibrations in the range 1700–2350 cm\textsuperscript{-1} are reported.

| mode | 49    | 50    | 51    | 52    | 53    | 54    |
|------|-------|-------|-------|-------|-------|-------|
| frequency | 1739.29 | 1920.37 | 2019.44 | 2082.33 | 2163.48 | 2176.49 |
| symmetry | b      | b     | a     | a     | a     | b     |
| IR active? | YES    | YES   | YES   | YES   | YES   | YES   |
| |dDIP/dQ| (a.u.) | 0.0132 | 0      | 0      | 0      | 0.0096 |
| intensity (km/mol) | 310.75 | 0     | 0     | 0      | 0      | 163.87 |
| intensity (%) | 100    | 0     | 0     | 0      | 0      | 52.73  |
| Raman active? | YES    | YES   | YES   | YES   | YES   | YES   |
| reduced mass (g/mol) | 11.72  | 11.975 | 11.977 | 11.998 | 11.806 | 11.844 |
Full Cartesian coordinates and energies for the optimized structures of $S_0$, $S_1$ and $T_1$ at B3LYP/cc-pVTZ are reproduced below.

$S_0$, B3LYP/cc-pVTZ

| X     | Y     | Z     |
|-------|-------|-------|
| 0.00000000 | 0.00000000 | 15.99285951 |
| 0.00000000 | 0.00000000 | 13.25506694 |
| 0.00000000 | 0.00000000 | 10.96533592 |
| 0.00000000 | 0.00000000 |  8.41612125 |
| 0.00000000 | 0.00000000 |  3.57801580 |
| 0.00000000 | 0.00000000 |  1.26193635 |
| 0.00000000 | 0.00000000 | -15.99285951|
| 0.00000000 | 0.00000000 | -13.25506694|
| 0.00000000 | 0.00000000 | -10.96533592|
| 0.00000000 | 0.00000000 |  -8.41612125|
| 0.00000000 | 0.00000000 |  -6.10649313|
| 0.00000000 | 0.00000000 |  -3.57801580|
| 0.00000000 | 0.00000000 |  -1.26193635|
| 0.00000000 | 0.00000000 |   6.10649313|

E(SCF) = -536.6437611393 Hartree
E(ZPE) =  0.1336094 Hartree
E(SCF) + E(ZPE) = -536.5101517 Hartree

$S_1$, TD-B3LYP/cc-pVTZ

| X     | Y     | Z     |
|-------|-------|-------|
| 0.00000000 | 0.00000000 | 15.97913943 |
| 0.00000000 | 0.00000000 | 13.24766966 |
| 0.00000000 | 0.00000000 | 10.93440726 |
| 0.00000000 | 0.00000000 |  8.4309487  |
| 0.00000000 | 0.00000000 |  3.61707559 |
| 0.00000000 | 0.00000000 |  1.21111600 |
| 0.00000000 | 0.00000000 | -15.97913943|
| 0.00000000 | 0.00000000 | -13.24766966|
| 0.00000000 | 0.00000000 | -10.93440726|
| 0.00000000 | 0.00000000 |  -8.4309487 |
| 0.00000000 | 0.00000000 |  -6.06061762|
| 0.00000000 | 0.00000000 |  -3.61707559|
| 0.00000000 | 0.00000000 |  -1.21111600|
| 0.00000000 | 0.00000000 |   6.06061762|
| 0.34664255 | 1.89627667 | 16.72301006|

-1.81554504 -0.64793708  16.72301006 h
0.34664255 1.89627667  16.72301006 h
1.46890249  -1.24833959  16.72301006  h
-1.81554504   0.64793708  -16.72301006  h
1.46890249   1.24833959  -16.72301006  h
0.34664255   -1.89627667  -16.72301006  h

E(SCF) = -536.6305863926 Hartree
E(excitation) = 0.064592026844 Hartree
E(ZPE) = 0.1295598 Hartree
E(SCF) + E(excitation) + E(ZPE) = -536.4364346 Hartree

T_{15, UB3LYP/cc-pVTZ}
-15.98284081   0.00613404   0.03610377  c
-13.24938981  -0.01188125   0.01170469  c
-10.93610540  -0.01723523  -0.00758142  c
-8.43144134  -0.02178336  -0.02535630  c
-3.62047902  -0.01102175  -0.04869366  c
-1.20643479  -0.00242198  -0.05527171  c
-15.98284081  -0.00613404   0.03610377  c
 13.24938981   0.01188125   0.01170469  c
 10.93610540   0.01723523  -0.00758142  c
  8.43144134   0.02178336  -0.02535630  c
   6.05880970   0.01841455  -0.03822561  c
   3.62047902   0.01102175  -0.04869366  c
   1.20643479   0.00242198  -0.05527171  c
  -6.05880970  -0.01841455  -0.03822561  c
 -16.74267546  -0.02655004  -1.77674606  h
-16.71279772   1.90481534   0.39970513  h
-16.72057811  -1.24528408   1.50436118  h
  16.74267546   0.62655004  -1.77674606  h
  16.72057811   1.24528408   1.50436118  h
  16.71279772  -1.90481534   0.39970513  h

E(SCF) = -536.5787568201 Hartree
E(ZPE) = 0.1293849 Hartree
E(SCF) + E(ZPE) = -536.4493719 Hartree
Table S5. Comparisons of vibrational frequencies for dominant modes (as discussed in the main text) at the different levels of theory computed (B3LYP/6-31G**, B3LYP/cc-pVTZ, PBE0/6-31G**, PBE0/cc-pVTZ). Frequencies are given in cm$^{-1}$, uncorrected. Intensities are given in km/mol.

|        | B3LYP/6-31G** | B3LYP/cc-pVTZ | PBE0/6-31G** | PBE0/cc-pVTZ |
|--------|---------------|---------------|--------------|--------------|
|        | Frequency     | Intensity     | Frequency    | Intensity    | Frequency    | Intensity    | Frequency    | Intensity    |
| $S_0$  | 2274.95       | 68.69         | 2262.03      | 81.28        | 2305.94      | 53.38        | 2294.92      | 61.01        |
|        | 2311.21       | 237.37        | 2299.02      | 257.14       | 2342.98      | 328.89       | 2329.37      | 348.52       |
| $S_1$  | 1890.29       | 237.27        | 1860.44      | 258.13       | 1891.63      | 243.84       | 1862.19      | 381.91       |
|        | 2207.21       | 158.04        | 2191.96      | 185.55       | 2239.95      | 191.09       | 2220.37      | 216.13       |
| $T_1$  | 1836.45       | 277.46        | 1739.29      | 310.75       | 1838.66      | 408.00       | 1806.79      | 441.19       |
|        | 2190.29       | 139.22        | 2176.49      | 163.87       | 2214.02      | 190.63       | 2199.70      | 218.82       |