

Conjugation through Si-O-Si bonds, silsesquioxane (SQ) half cage copolymers, extended examples via SiO_{0.5}/SiO_{1.5} units. Multiple emissive states in violation of Kasha's Rule

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Supporting Information

Experimental section

Materials

All purchased chemicals were used as received unless otherwise indicated. Tetra(vinyldimethylsiloxy) capped half cage were synthesized by standard methods¹ and provided by the Unno laboratories. Bis(tri-tert-butylphosphine)palladium(0) (Pd[P(t-Bu)₃]₂), N,N-dicyclohexylmethylamine (NCy₂Me) and 1,4-dibromobenzene were purchased from TCI chemicals-Japan. 1,8,9-Trihydroxyanthracene, 4,4'-dibromo-1,1'-biphenyl, 4,4''-dibromo-p-terphenyl, 2,5-dibromothiophene, bromobenzene, 2-bromothiophene were purchased from Sigma Aldrich. Tetrahydrofuran was dried over pre-treated molecular sieves for at least 48h before use.

Synthetic Methods

(1) General procedure for oligomerization of Vy₄HC with Br-Ar-Br.

To a 50 mL flame-dried Schlenk flask under N₂, a mixture of Vy₄HC (0.2 mmol, 0.183 g), NCy₂Me (0.161 g, 0.8 mmol) and Br₂-Ar (0.2 mmol) in 10 mL dry THF was added. Further, Pd[P(t-Bu)₃]₂ (7.8 mg, 0.015 mmol) was added, and the flask connected to a condenser sealed with a rubber septum. Five cycles of vacuum-nitrogen were applied to ensure purity of the internal atmosphere. The mixture was stirred magnetically at reflux for 24 h and then cooled down. Furthermore, a 5 cm silica gel column using DCM as eluent was prepared and the reaction product was passed through using UV light to track the traces of the product in the column and the solution. The eluted product was solvent-reduced via rotary evaporation, then dried under vacuum at 60 °C to obtain a waxy substance that was further characterized.

(2) General procedure for capping of Vy₄HC with Ar-Br

To a 50 mL flame-dried Schlenk flask under N₂, a mixture of Vy₄HC (0.2 mmol, 0.278 g), NCy₂Me (0.161 g, 0.8 mmol) and Br-Ar (0.88 mmol, 10 % molar excess with respect to the amount needed to couple with the four vinyl groups of the SiT₄ half cage) in 10 mL dry THF was added. Further, Pd[P(t-Bu)₃]₂ (7.8 mg, 0.015 mmol) was added, and the flask connected to a condenser sealed with a septum. Five cycles of vacuum-nitrogen were applied to ensure purity of the internal atmosphere. The mixture was stirred magnetically at reflux for 24 h and then cooled down. Furthermore, a 5 cm silica gel column using DCM as eluent was prepared and the reaction product was passed through using UV light to track the traces of the product in the column and the solution. The volume of the eluted product was reduced via rotary evaporation, then dried under vacuum at 60 °C giving waxy substance characterized as recorded above.

(3) Column chromatographic separation the Vy₄HC-coStil oligomers mixture by DP.

Before the column chromatography, TLC was done to determine the proper solvent combination. For the combination of hexane and DCM with the ratio of 5:1, it shows a good separation effect of the monomers and dimers and trimers therefore this ratio was used as the starting solvent combination. As the short oligomers were washed out, the polarity of the solvent was increased until all DCM. A 20 cm long column was prepared using 50 g silica gel (230-450 mesh) and a solvent system of hexane and DCM, with the ratio described before, was used to separate the polymer according to the chain length. During the column chromatography, clear group of products can be seen under 365 nm black light illumination.

Analytical methods

(1) Matrix-Assisted Laser Desorption/Time of flight Spectrometry (MALDI-ToF)

The MALDI-ToF analyses were performed on a Bruker Autoflex Speed MALDI-ToF equipped with a 337 nm nitrogen laser in positive-ion reflection mode using 1,8,9-Trihydroxyanthracene, 97%, as matrix, and AgNO₃ as ion source. Samples were prepared by mixing solutions of 5 parts matrix (10 mg/mL), 5 parts sample (1 mg/mL in THF), and 1-part AgNO₃ (1 mg/mL in water).

The mixture was blotted in three different spots of a steel plate with different concentrations before conducting the analyses under high vacuum.

(2) Fourier Transform Infrared Spectroscopy

The FTIR analyses were carried out using a Nicolet 6700 Spectrometer from Thermo Scientific in transmission mode. Approximately 4 mg of sample were mixed in a mortar with 400 mg of KBr and compressed into a sample holder. The spectra were collected for the mixtures and for a background of pure grinded KBr in the range from 400 to 4000 cm^{-1} .

(3) Thermogravimetric analysis (TGA)

The TGA analyses were performed in a SDT Q600 machine from TA instruments. The analyses were carried out by heating approximately 10 mg of sample from 50 to 900 °C at 10°C per min using aluminum pans, previously cleaned by soaking in *aqua regia*, distilled water and ethanol. The carrier gas was dry air at 60 ml/min.

(4) Nuclear Magnetic Resonance (NMR)

The analyses were carried out in a VarianM400 operated at 400 MHz (9.4 Tesla) Premium Shielded Magnet. The solvent used was deuterated chloroform containing 100 ppm TMS unless indicated otherwise. The analyses were performed by scanning 24 times in concentrations around 10 mg per mL for proton detection and 50 mg per mL for carbon. Simulations were performed using Chem Draw office suite, license by University of Michigan.

(5) Gel permeation chromatography (GPC)

The GPC analyses were performed in a waters 515 GPC with in-line degasser and THF as solvent. The samples were prepared by diluting approx. 2 mg of sample into 1 mL THF and filtering through PVDF filters of 0.22 microns pores. The Refraction Index detector registered all the products eluting out of the column for 50 min. The estimation of molar masses is given by an internal calibration using PS standard solutions with narrow dispersity.

(6) Quantum yield measurements.

Quantum yields were measured using an integrated sphere. Samples were dissolved in CH_2Cl_2 (DCM) and diluted to a concentration (10^{-3} - 10^{-4} M) where the absorption maximum was <10% for a 1 cm path length. Absorption and emission inside the sphere were determined by comparison to a blank CH_2Cl_2 in cuvette (glass only). Each sample was measured three times or more.

(7) 2D absorption-emission spectral maps²

One-photon (linear) excitation-emission spectra were acquired using Perkin-Elmer spectrofluorimeter LS-50B. The sample solution was contained in a 10x10mm quartz spectroscopic cuvette using ACN as the solvent. To minimize artifacts due to potential internal filter effect the peak absorbance of the solute was kept below, O.D. < 0.15. The cuvette filled with neat ACN was checked for potential background emission, which was found to contribute only insignificantly compared to the signals collected from the sample.

Two-photon excitation and corresponding emission spectra were acquired using a technique described in detail in [xx]. Briefly, the 2-photon excitation source comprised a femtosecond optical parametric amplifier (OPA, Orpheus-HE, Light Conversion Ltd.) that was pumped by a diode-pumped, 6 kHz pulse repetition rate, femtosecond regenerative laser amplifier (Pharos-SP, Light Conversion Ltd.). The OPA produced ~200-fs duration pulses with the energy of 50 - 150 μJ , 7 - 16 nm spectral band width, and with the pulse wavelength tunable in the range, $\lambda_{2\text{PA}} = 630 - 1040$ nm. The OPA output pulses were appropriately spectrally filtered, attenuated and focusses on the sample contained in 10x10mm spectroscopic cuvette. Concentration of the solute in DMSO was in the range, 0.01–0.1 mM. The two-photon excited fluorescence (2PEF) emission from the sample was collected at 90° and focused into a spectrograph (Kymera 328i, Andor), which recorded the

emission spectrum in the range, at each excitation wavelength, $\lambda_{\text{em}} = 400 - 650$ nm, using a liquid nitrogen cooled CCD detector (Symphony Solo, Horiba) at each excitation wavelength, $\lambda_{2\text{PA}}$. Quadratic dependence of the 2PEF signal was checked at each $\lambda_{2\text{PA}}$ wavelength by measuring the emission intensity at a range of different excitation pulse energies to yield power-law dependence of 2.0 ± 0.1 .

Modeling methods:

(1) Ground state optimized structures of all structures were determined using DFT at the B3LYP/6-31G(d,p) level of theory with GD3BJ dispersion correction. The vertical excitation energies and electronic absorption spectra were investigated using time dependent density functional theory (TD-DFT) with hybrid exchange-correlation functionals CAM-B3LYP. All calculations were run with Gaussian 16 program package.

Synthesis of Vy_4HC -copolymers and model compounds

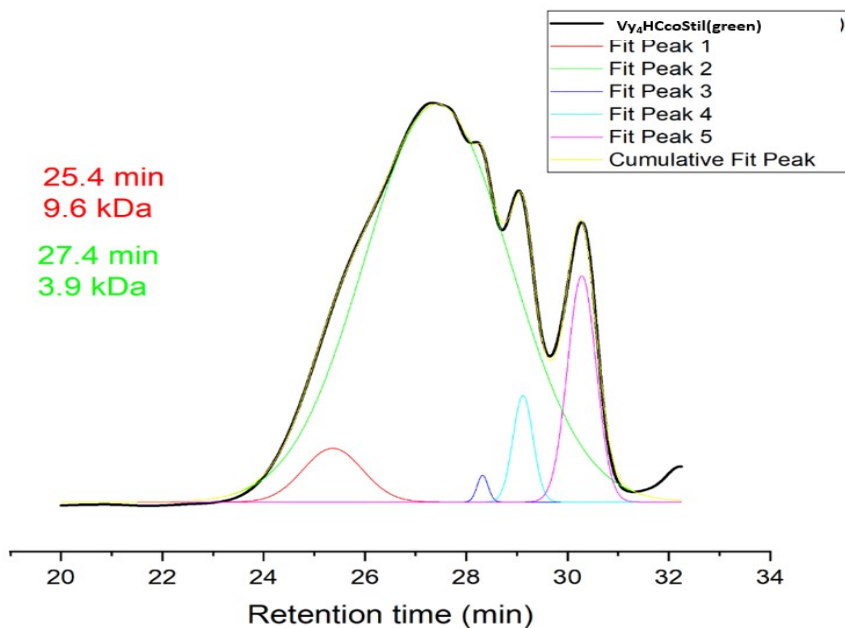


Figure S1. GPC chromatogram for the Vy_4HC -coStil (green fraction) (black) and the deconvoluted peaks (colors). The value of M_n is estimated from GPC software.

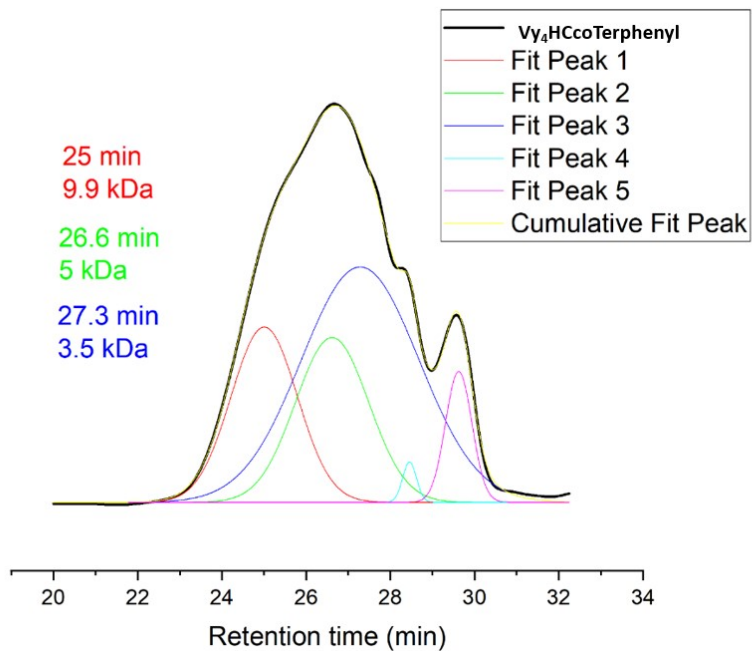


Figure S2. GPC chromatogram for the Vy_4HC -coTerph (black) and the deconvoluted peaks (colors). The value of M_n is estimated from GPC software.

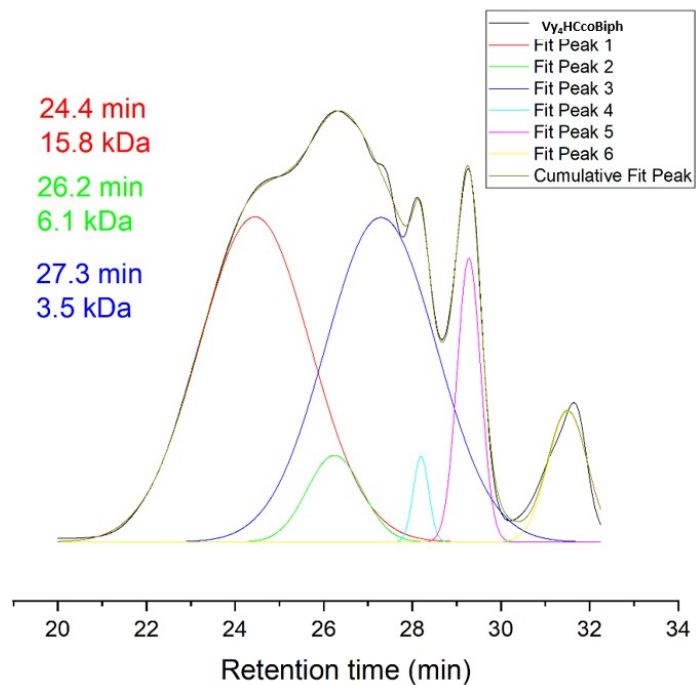


Figure S3. GPC chromatogram for the $Vy_4HC-coBiph$ (black) and the deconvoluted peaks (colors). The value of M_n is estimated from GPC software.

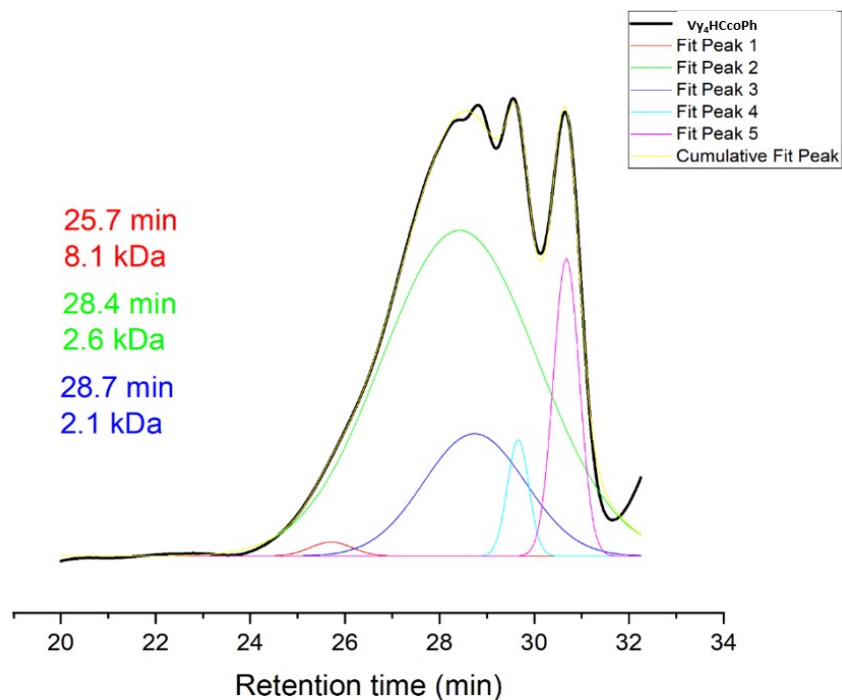


Figure S4. GPC chromatogram for the $Vy_4HC-coPh$ (black) and the deconvoluted peaks (colors). The value of M_n is estimated from GPC software.

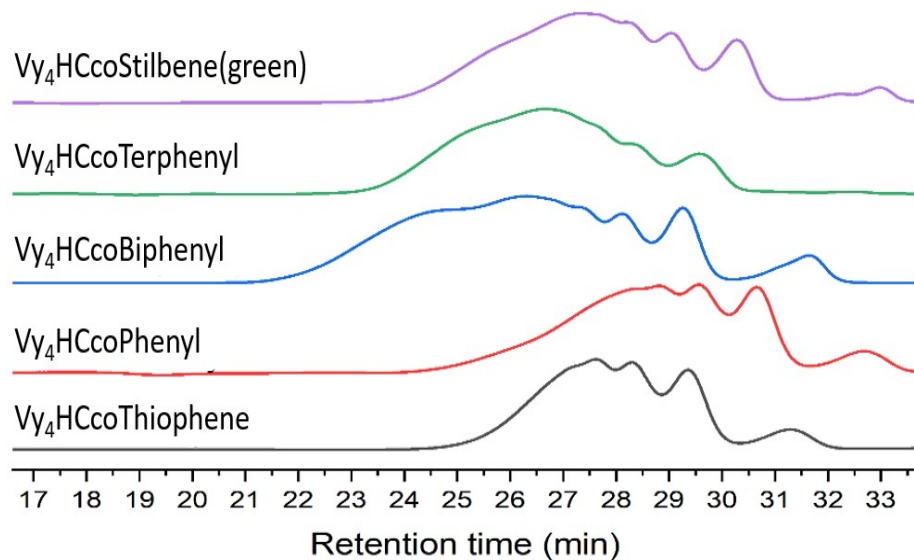


Figure S5. Stacked GPC traces of the Vy_4HC -copolymers. Intensities are normalized and limited to 15-34 min.

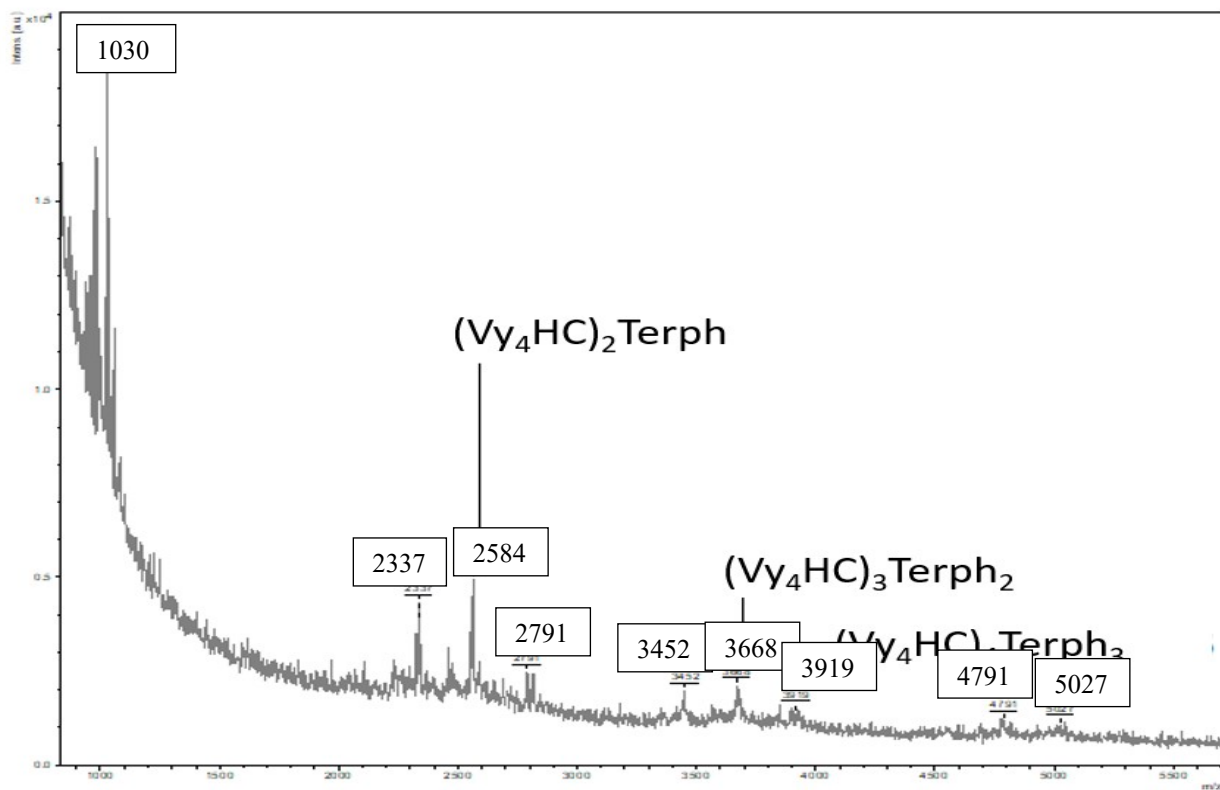


Figure S6. MALDI of Vy_4HC -coTerph.

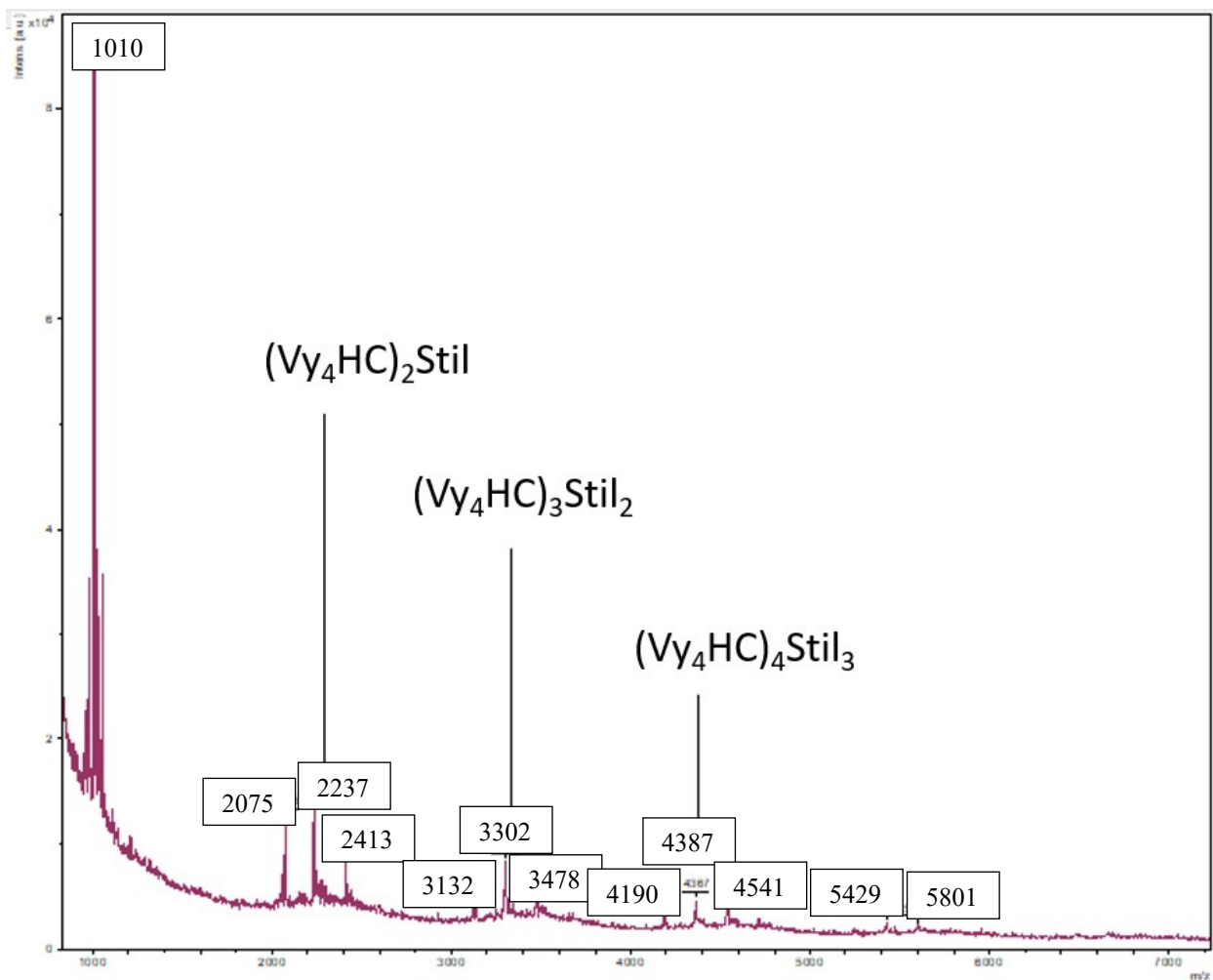


Figure S7. MALDI of Vy_4HC -coStil.

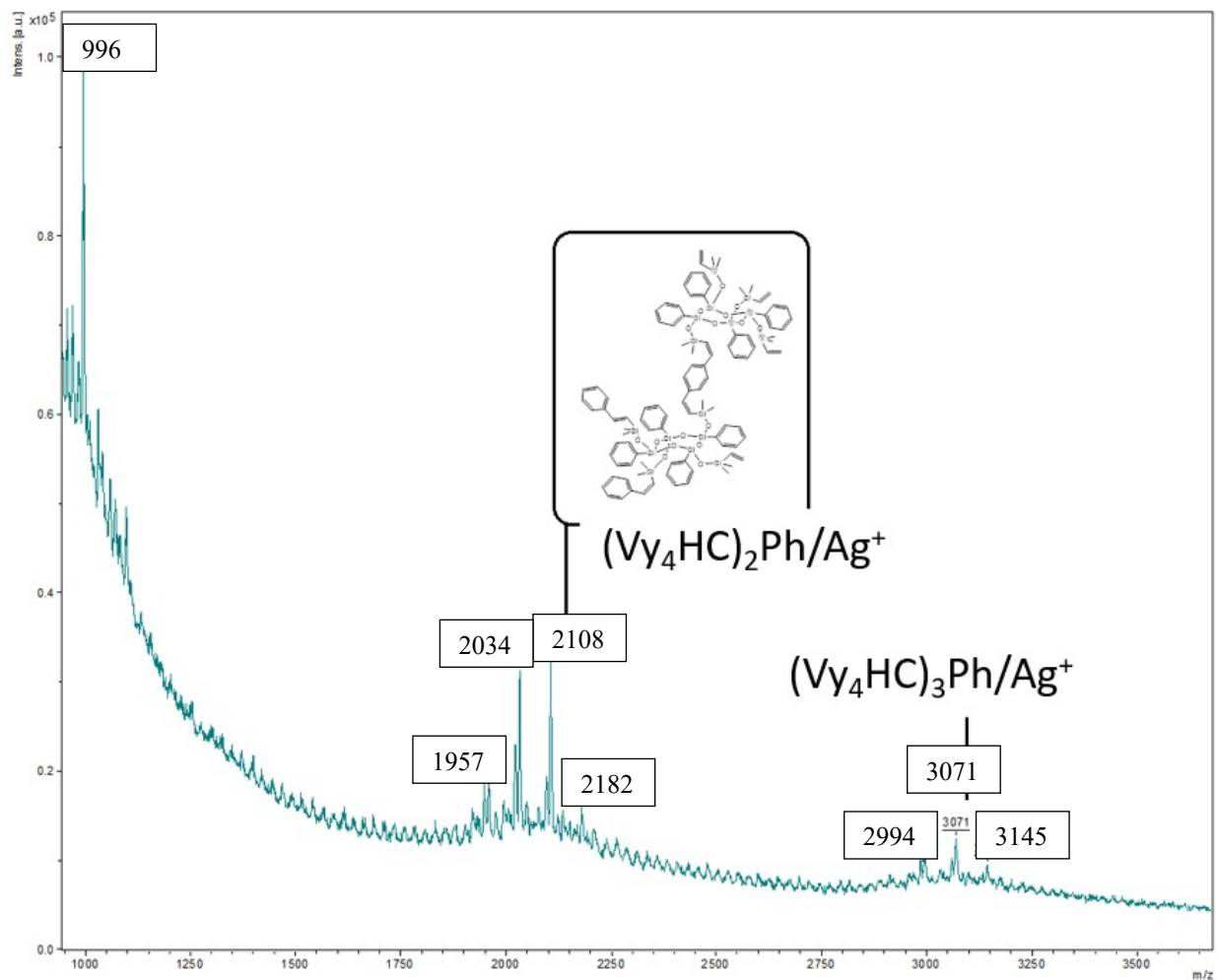


Figure S8. MALDI of $Vy_4HC-coPh$.

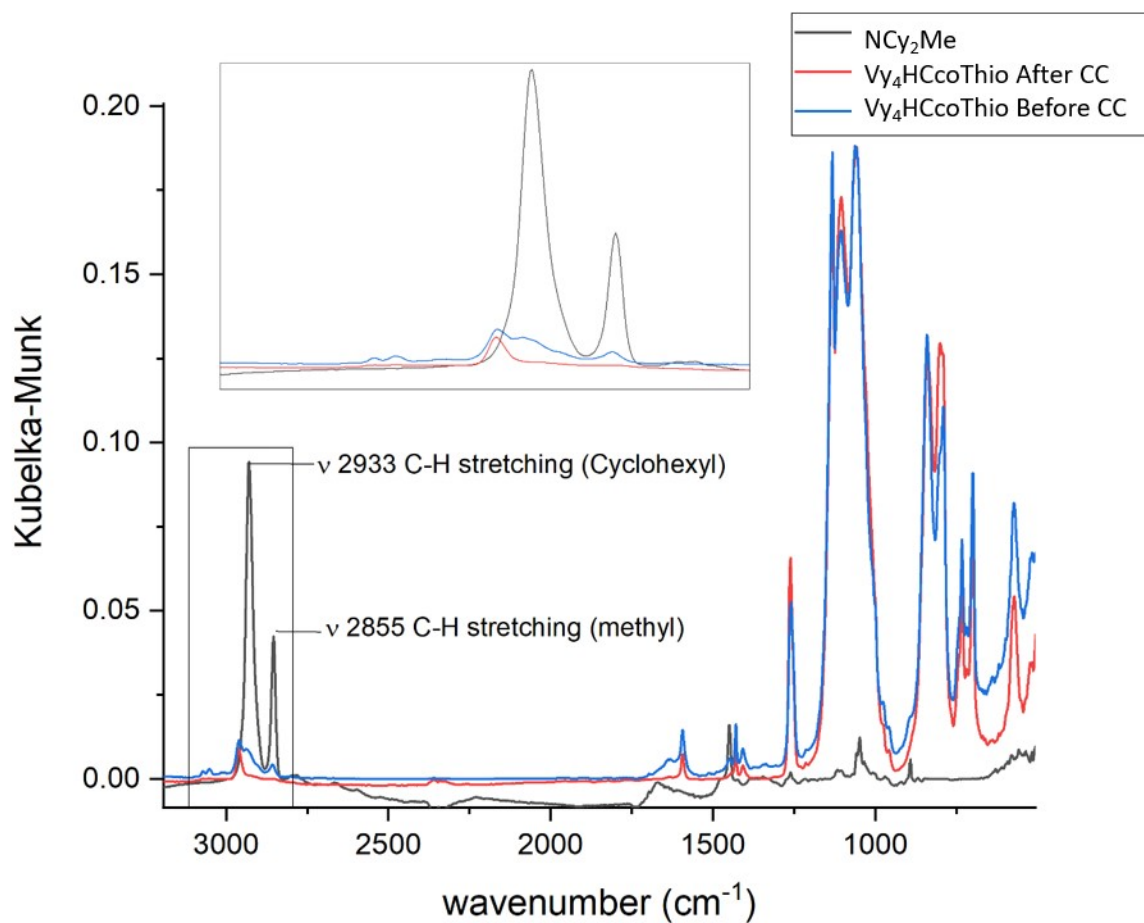


Figure S9. FTIR comparison of the $\text{Vy}_4\text{HC-coThio}$ oligomer before and after CC purification and the spectrum of pure NCy_2Me .

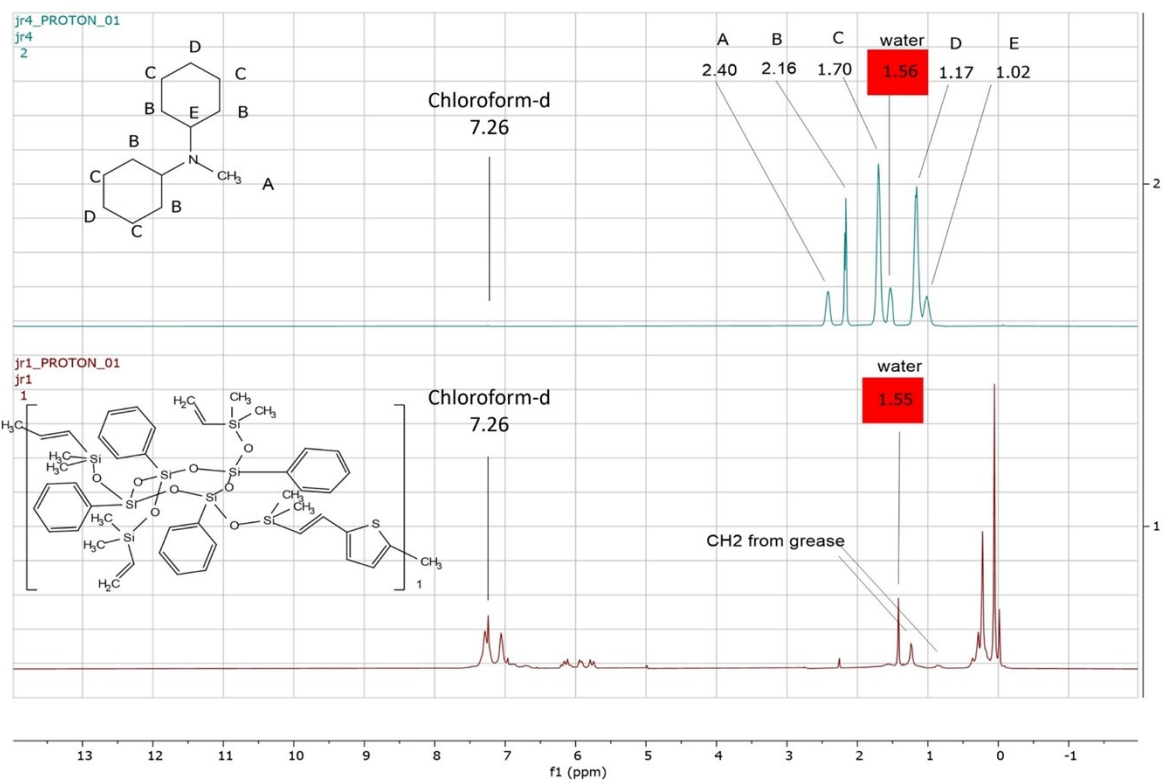


Figure S10. ^1H NMR comparison of the $\text{V}_4\text{HC-coThio}$ and $\text{N}(\text{Cy})\text{Me}_2$ taken in CDCl_3 . Top: Spectrum and structure of the $\text{N}(\text{Cy})\text{Me}_2$. Bottom: spectrum and structure of the $\text{N}(\text{Cy})\text{Me}_2$ after purification, showing the expected peaks.

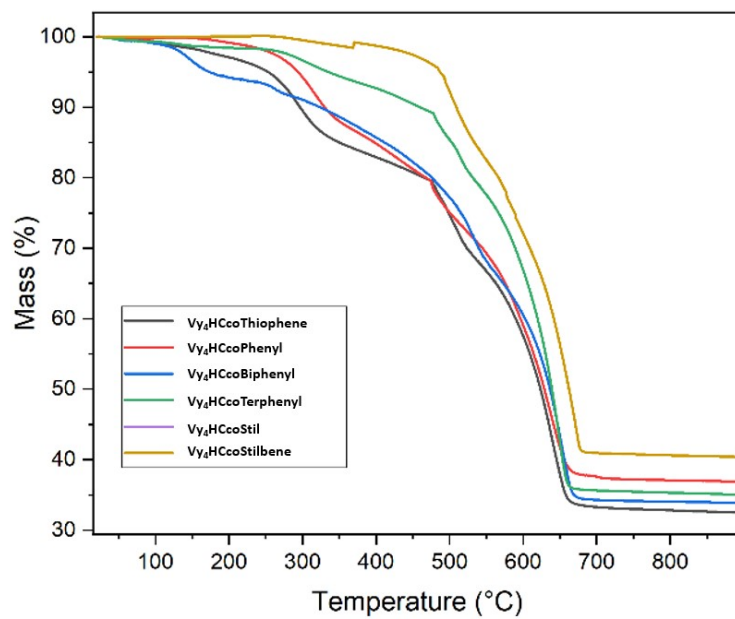


Figure S11. TGA for the produced Vy_4HC oligomers. Analyses performed using alumina pans from 50° to 800 °C/10 °C/min/air.

Photophysical characterization of Vy_4HC -copolymers and model compounds

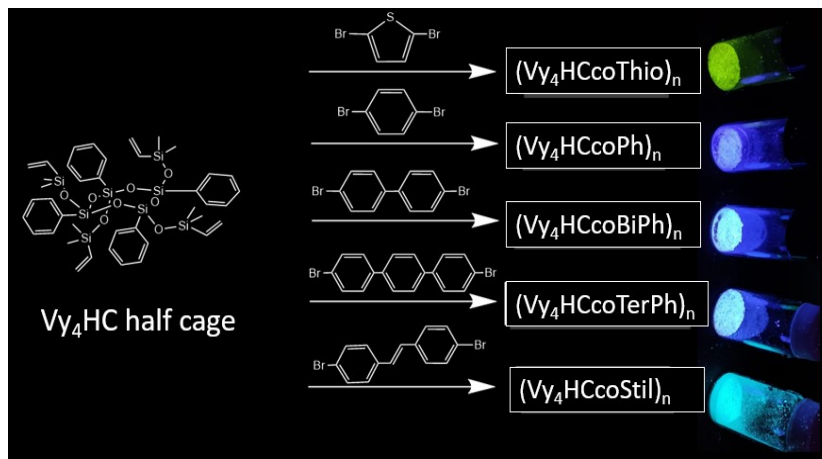


Figure 12. Fluorescence of solid Vy_4HC co-oligomers on excitation at 265 nm.

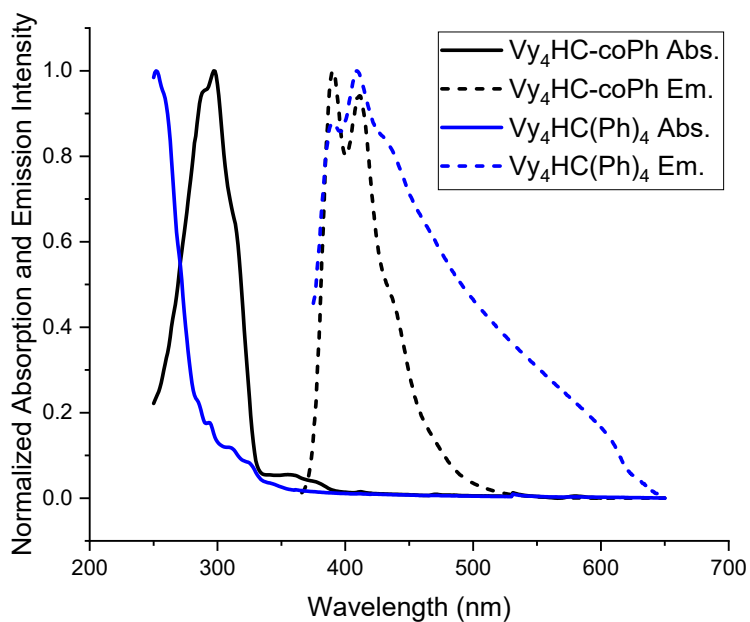


Figure S13. Normalized absorption and emission spectra for the Vy_4HC -coPh with its model compounds $Vy_4HC(Ph)_4$. Excitation at 265 nm in DCM.

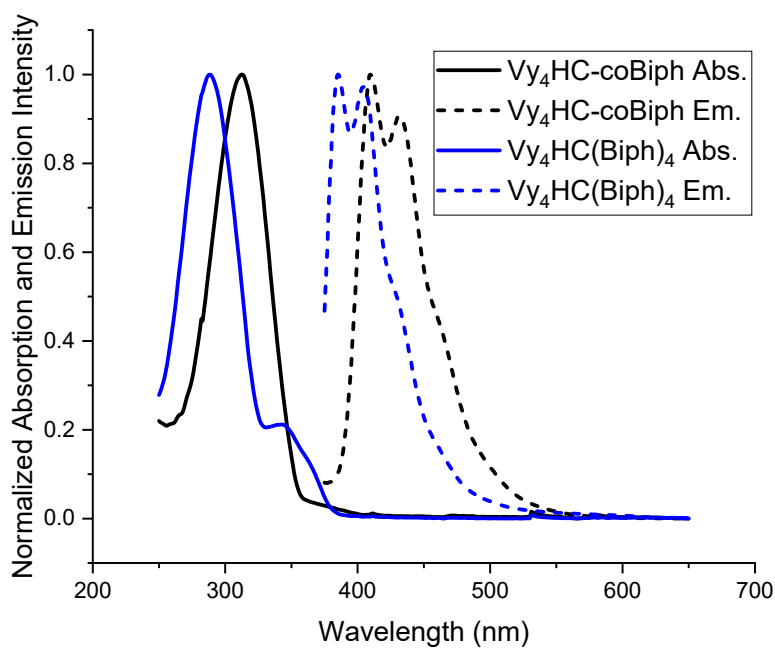


Figure S14. Normalized absorption and emission spectra for the $Vy_4HC-coBiph$ with its model compounds $Vy_4HC(Biph)_4$. Excitation at 265 nm in DCM.

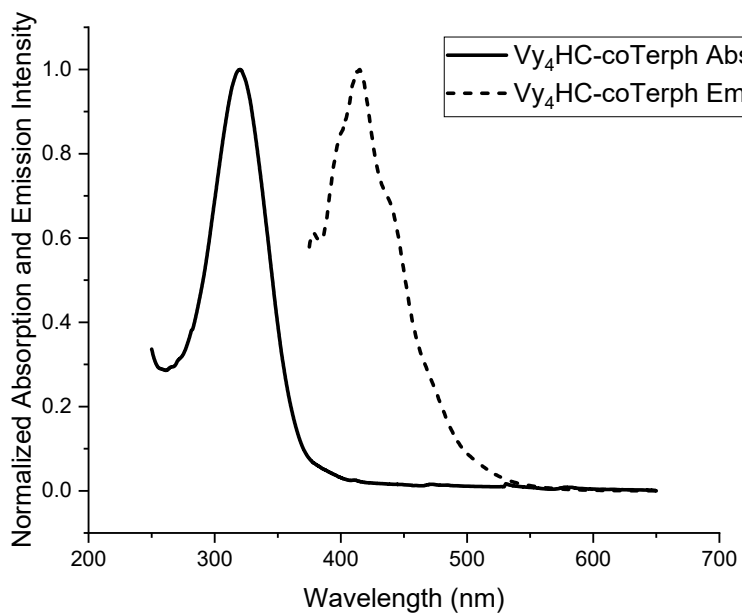


Figure S15. Normalized absorption and emission spectra for the $Vy_4HCcoTerph$. Excitation at 265 nm in DCM.

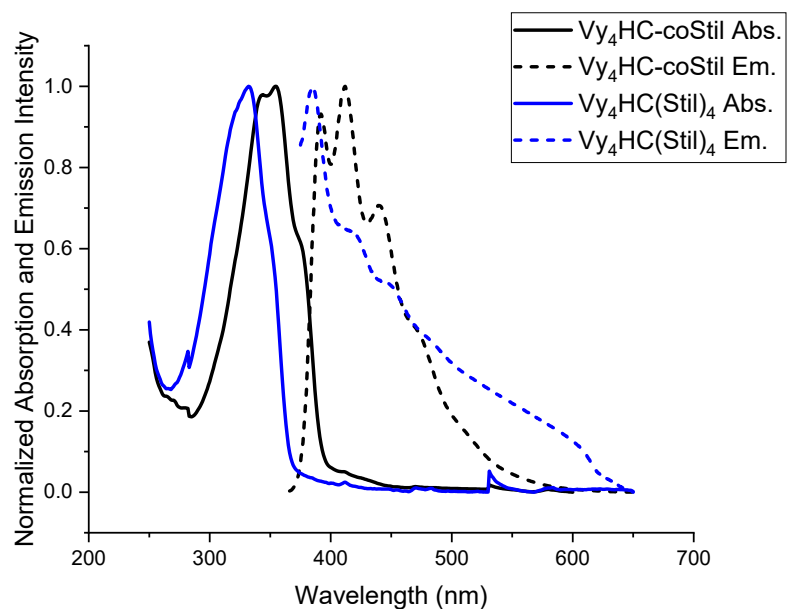


Figure S16. Normalized absorption and emission spectra for the Vy_4HC -coStil with its model compounds $Vy_4HC(Stil)_4$. Excitation at 265 nm in DCM.

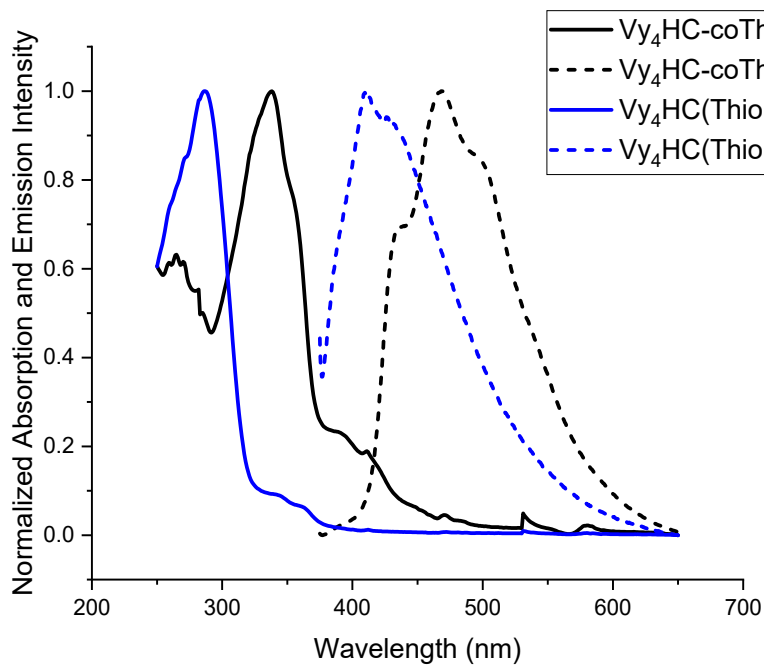


Figure S17. Normalized absorption and emission spectra for the Vy_4HC -coThio with its model compounds $Vy_4HC(Thio)_4$. Excitation at 265 nm in DCM.

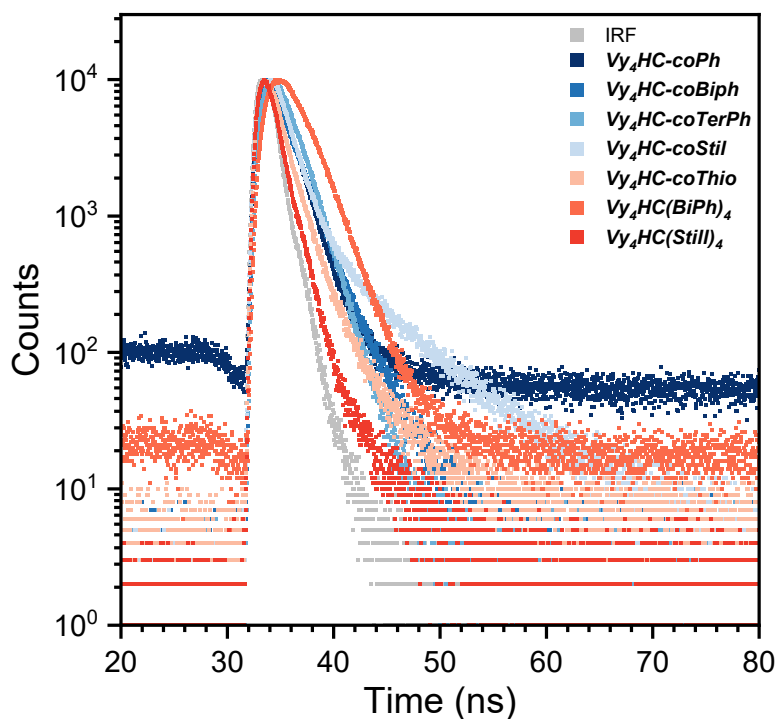


Figure S18. Excited state lifetime measurement of Vy_4HC copolymers and model compounds.

Table S1. Excited state lifetime measurement of Vy_4HC copolymers and model compounds.

		Absorption λ_{max} (nm)	Emission λ_{max} (nm)	E_{stokes} (nm)	Φ_F (%)	τ_1 (ns)	τ_2 (ns)	$\tau_{avg.}$ (ns)	k_r ($10^7 s^{-1}$)	k_{nr} ($10^7 s^{-1}$)
Copolymers	$Vy_4HC-coPh$	289, <u>297</u>	<u>390</u> , 411	93	86 ± 1	1.2	-	1.2	72	12
	$Vy_4HC-coBiph$	313	<u>409</u> , 432	96	88 ± 1	1.3	-	1.3	68	9.2
	$Vy_4HC-coTerPh$	320	415	95	75 ± 1	1.5	-	1.5	50	17
	$Vy_4HC-coStil$	344, <u>354</u>	<u>392</u> , <u>412</u> , 440	58	50 ± 3	1.5 (0.95)	7.3 (0.05)	1.8	28	28
	$Vy_4HC-coThio$	338	469	131	3 ± 0.2	0.08 (0.97)	1.8 (0.03)	1.2	2.5	81
Model compounds	$Vy_4HC(BiPh)_4$	288	<u>385</u> , 404	97	3 ± 0.5	2.1	-	2.1	1.4	46
	$Vy_4HC(Stil)_4$	332	385	53	1.2 ± 0.2	0.09 (0.99)	1.6 (0.01)	0.1	1	82

Radiative constant: $k_r = \Phi_F/\tau_{avg.}$, Non radiative constant: $k_{nr} = (1 - \Phi_F)/\tau_{avg.}$
 Quantum efficiency: Φ_F

The effect of DP on photophysics.

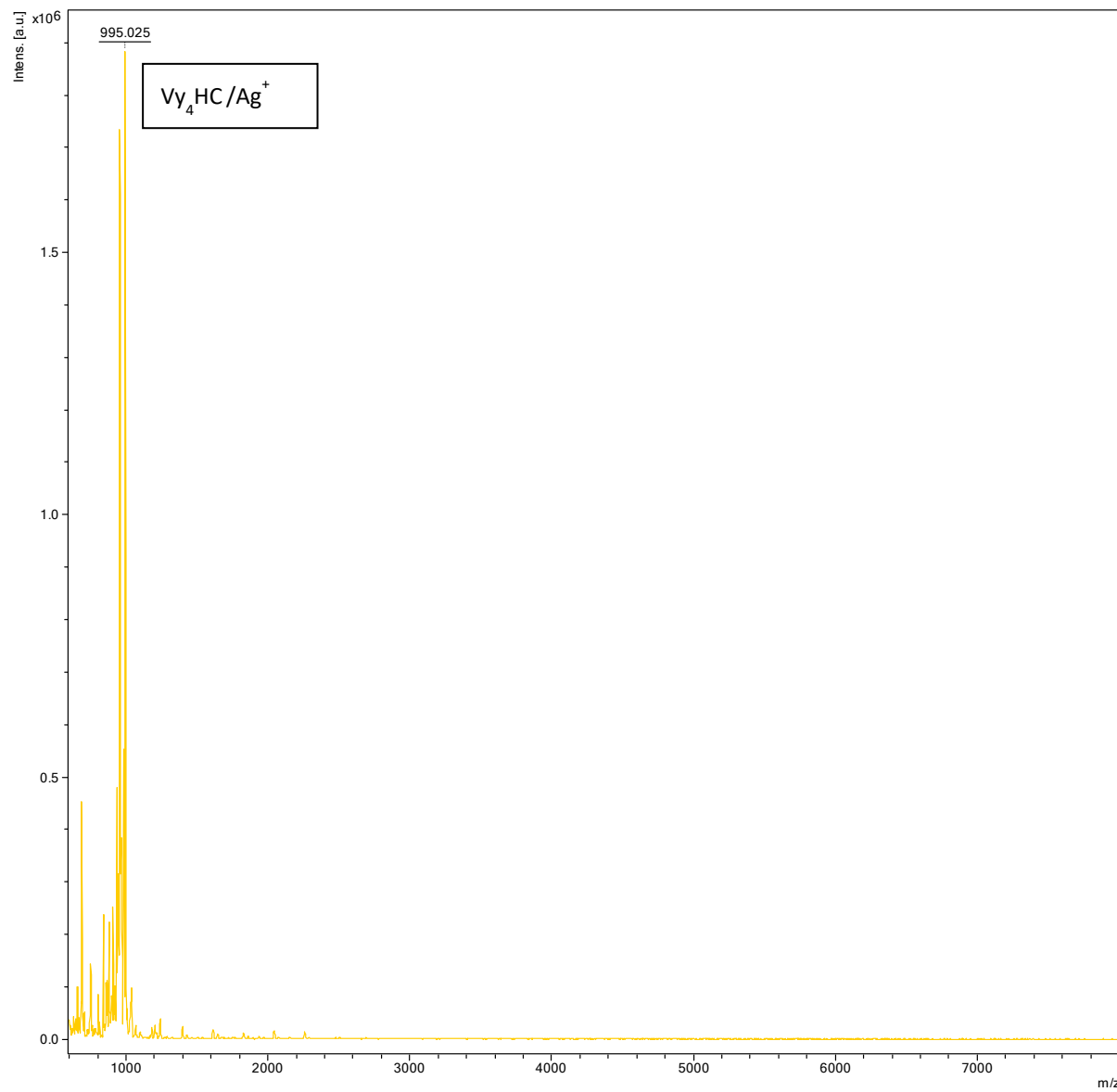


Figure S19. MALDI of product in Sample 27 of Vy₄HC-coStil after column chromatography showing starting material.

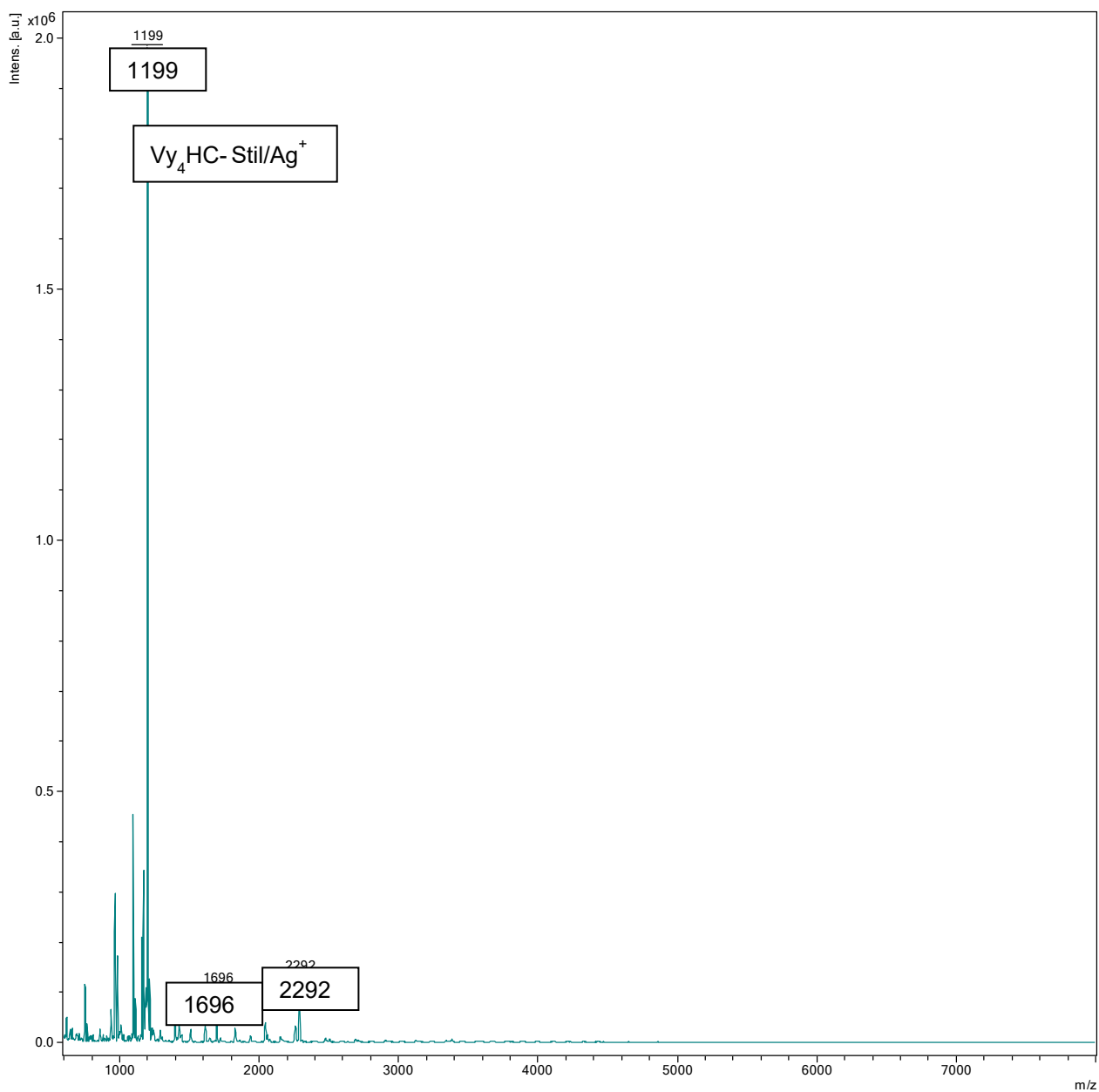


Figure S20. MALDI of product in sample 39 of Vy₄HC-coStil after column chromatography showing starting material plus one stilbene.

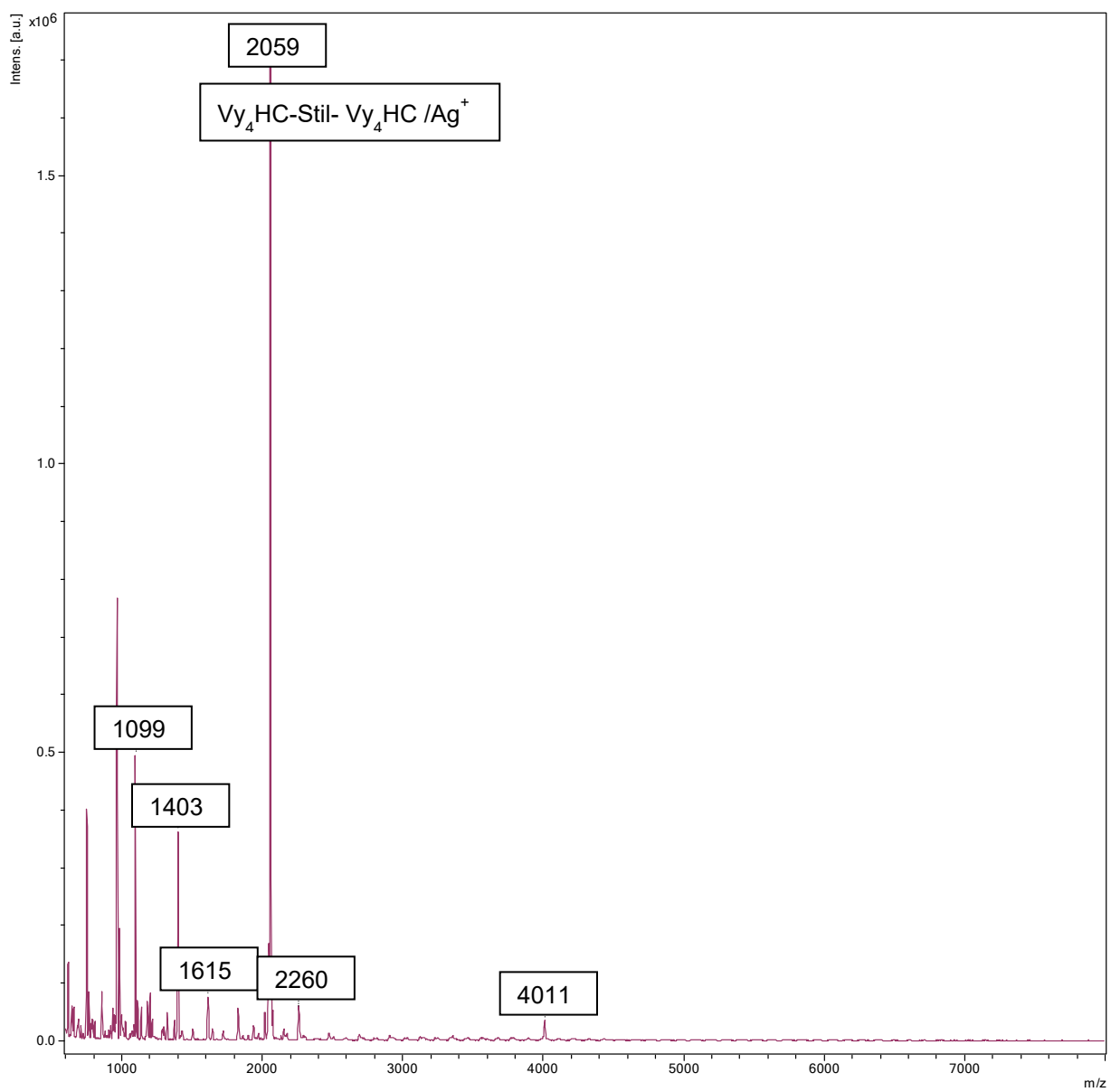


Figure S21. MALDI of product in sample 50 of Vy₄HC-coStil after column chromatography showing stilbene coupled to two half cages.

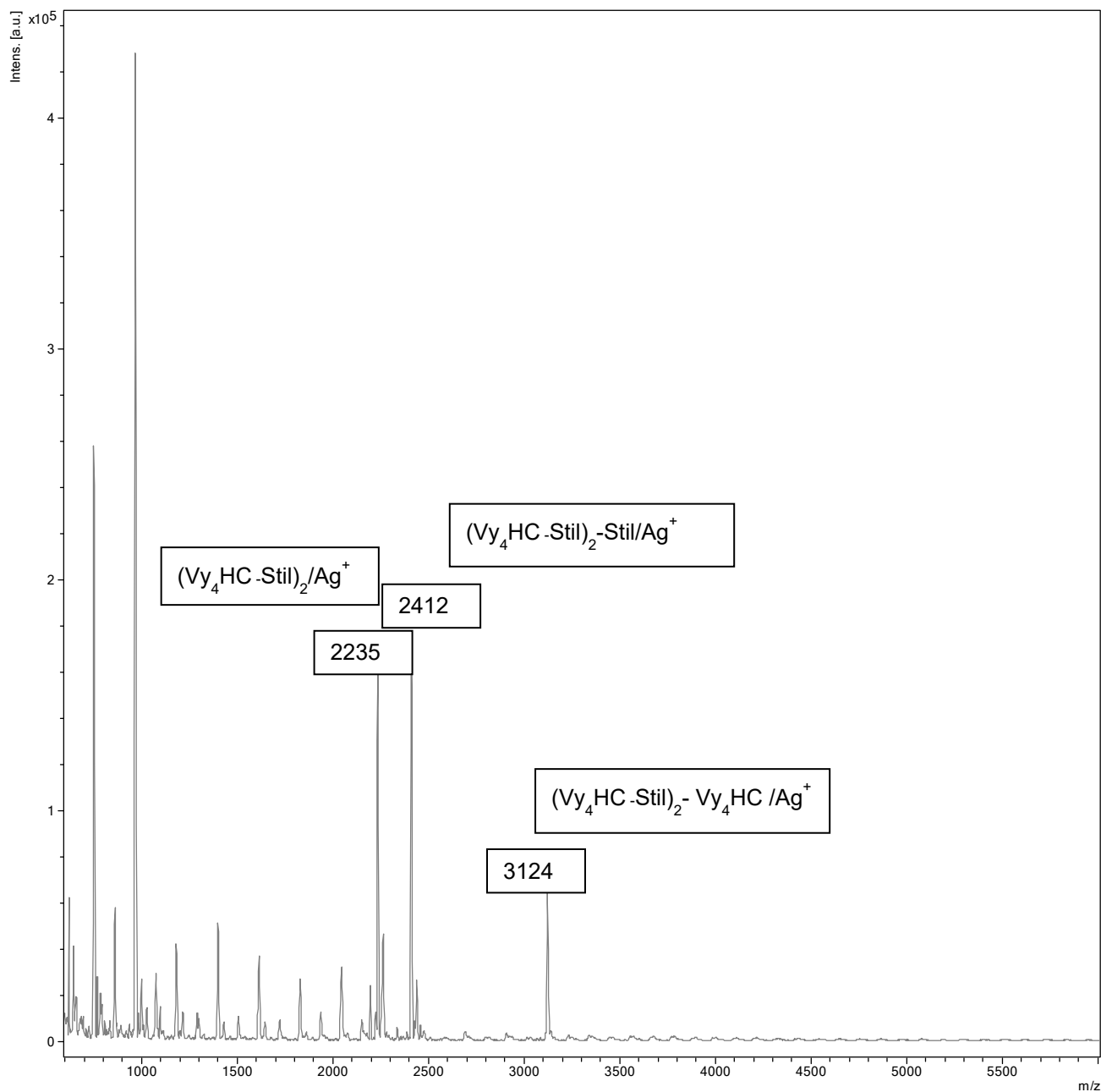


Figure S22. MALDI of product in sample 73 of Vy_4HC -coStil after column chromatography showing dimers and trimers.

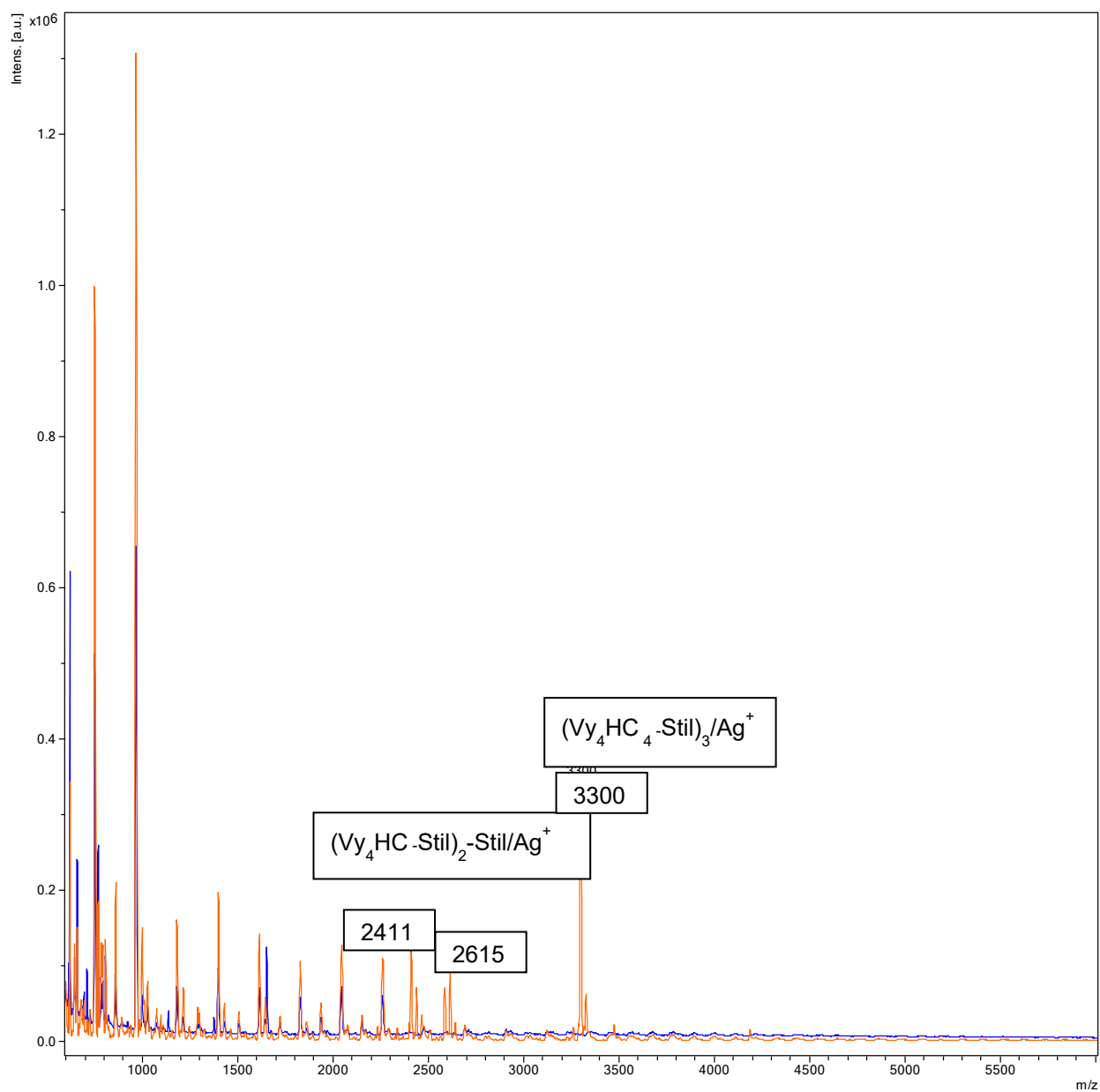


Figure S23. MALDI of product in sample 83 of Vy_4HC -coStil after column chromatography showing dimers and trimers.

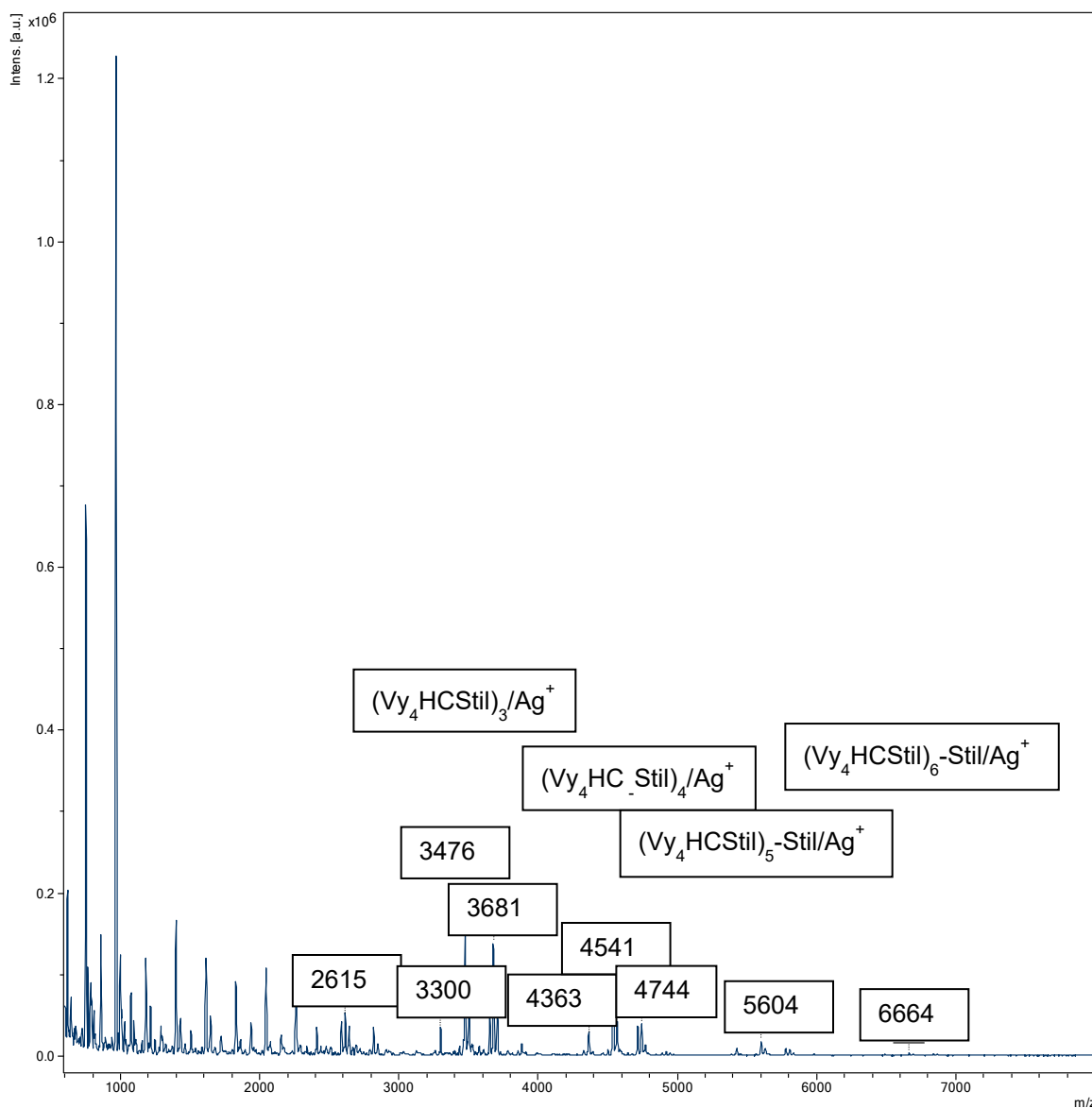


Figure S24. MALDI of product in Sample 91 of Vy_4HC -coStil after column chromatography showing trimers-hexamers. Note peak heights only correlate with facility to undergo ionization and are not a measure of mass fraction.

Charge Transfer (CT)

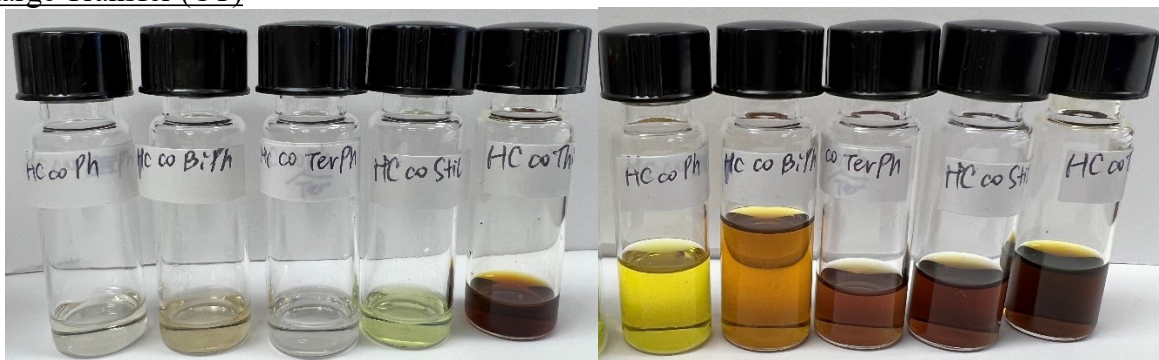


Figure S25. CT experiments with F₄TCNQ Vy₄HC copolymers. **a.** Vy₄HC copolymers in DCM. **b.** Vy₄HC copolymers with F₄TCNQ in DCM. (From left to right: Vy₄HC-coPh, Vy₄HC-coBiph, Vy₄HC-coTerph, Vy₄HC-coStil, Vy₄HC-coThio.)

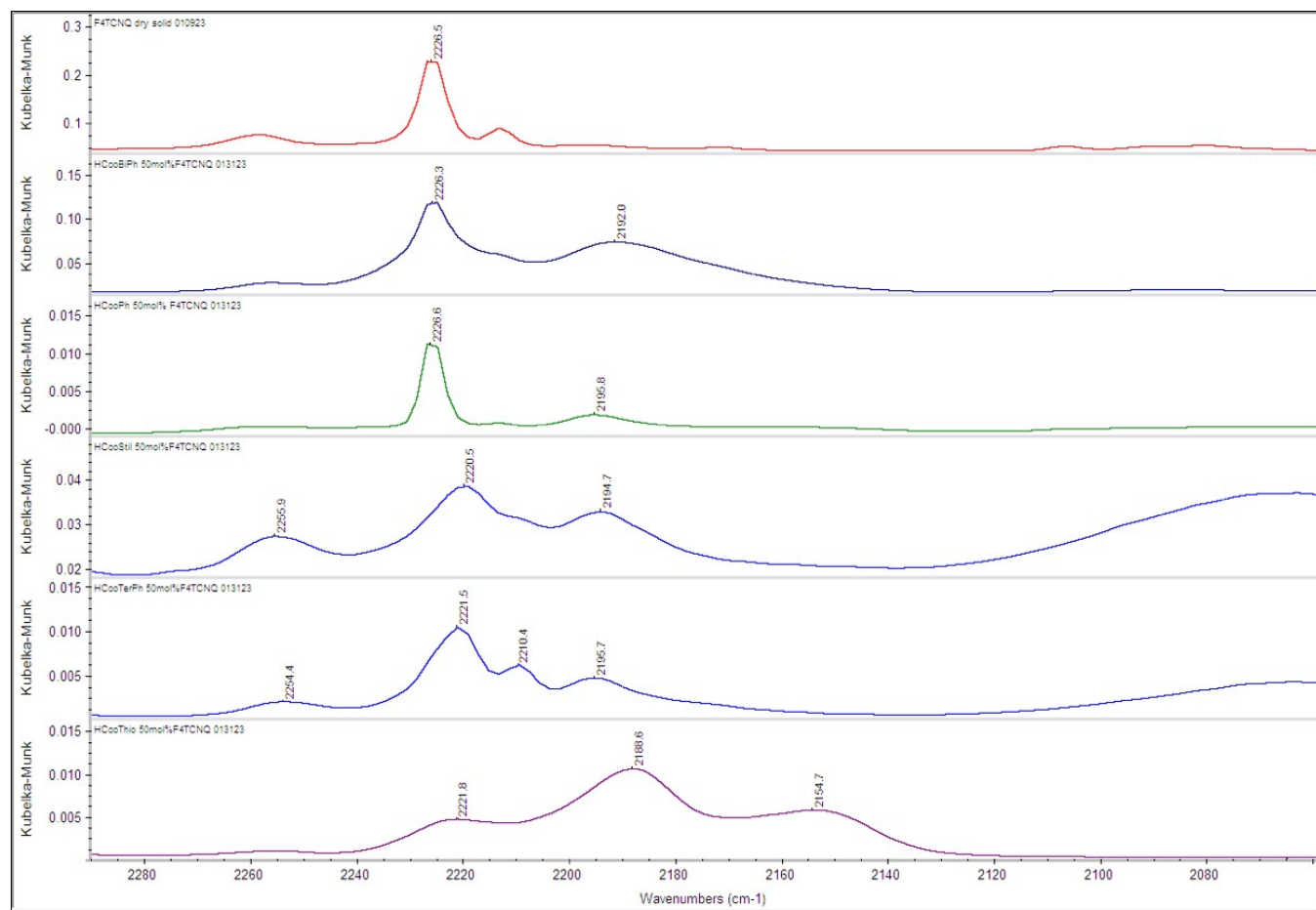


Figure S26. FTIR spectra of Vy₄HC co-polymers with F₄TCNQ. FTIR run in transmission mode by preparing KBr pellets of F₄TCNQ and Vy₄HC mixtures after letting stand 6 h.

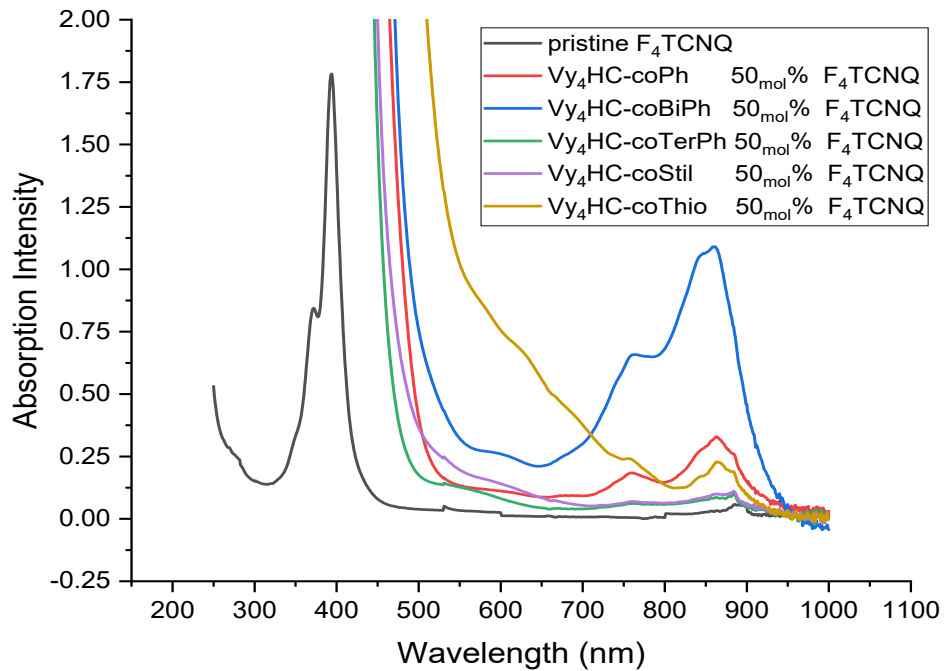


Figure S27. Absorption spectra for CT experiments of Vy₄HC copolymers with F₄TCNQ. The concentration of the F₄TCNQ is 2mg/ml in DCM. Vy₄HC copolymers DCM solution was prepared as 10 mg/ml.

Modeling studies

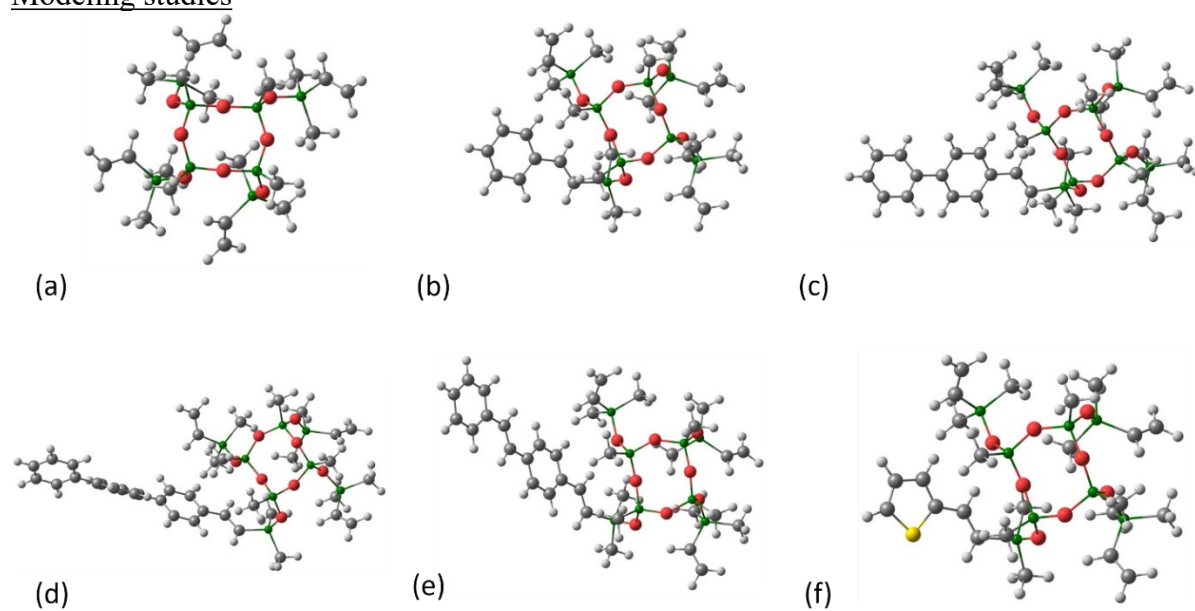


Figure S28. Optimized (a) Vy₄HC (b) Vy₄HC-coPh. (c) Vy₄HC-coBiph (d) Vy₄HC-coTerph (e) Vy₄HC-coStil (f) Vy₄HC-coThio structures.

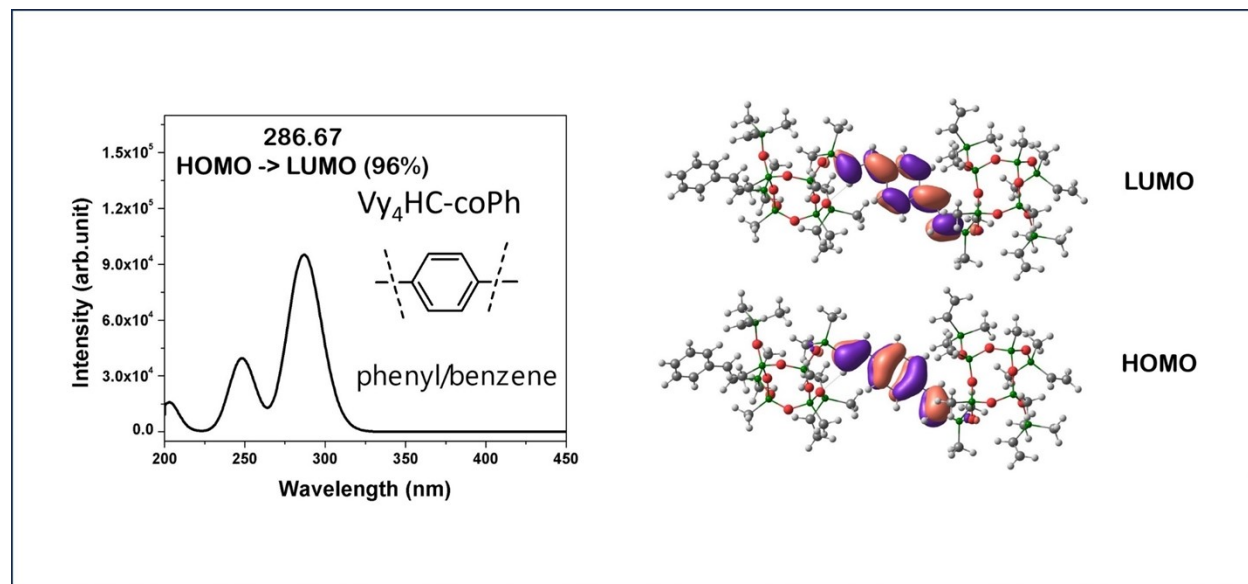


Figure S29. Calculated HOMO and LUMO and absorption spectra for the Vy₄HC-coPh.

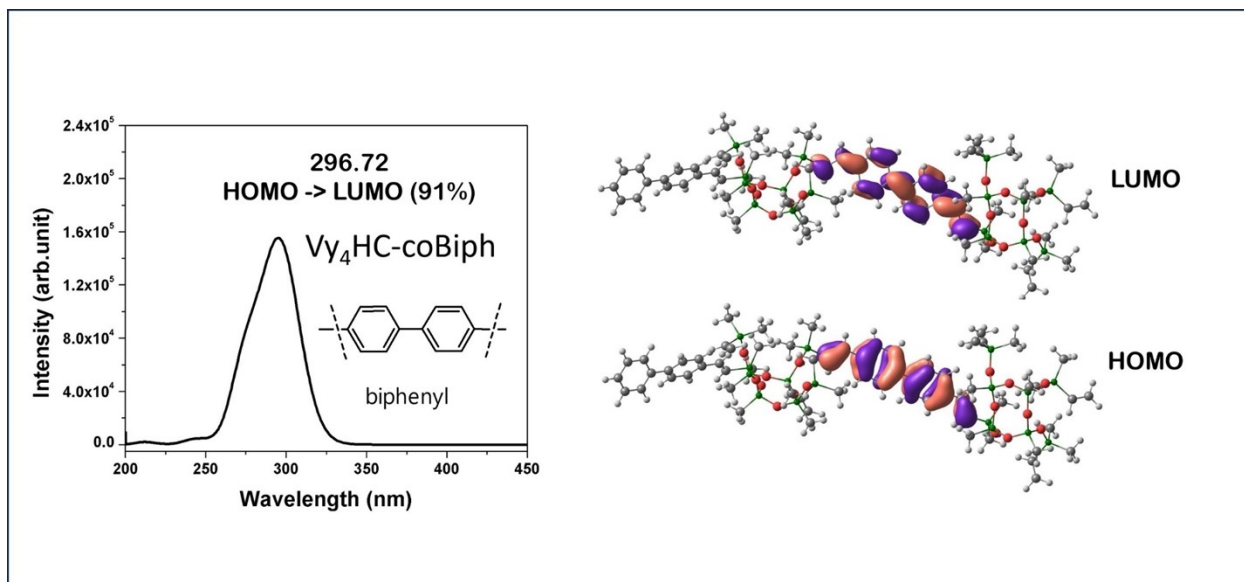


Figure S30. Calculated HOMO and LUMO and absorption spectra for the $Vy_4HC-coBiph$.

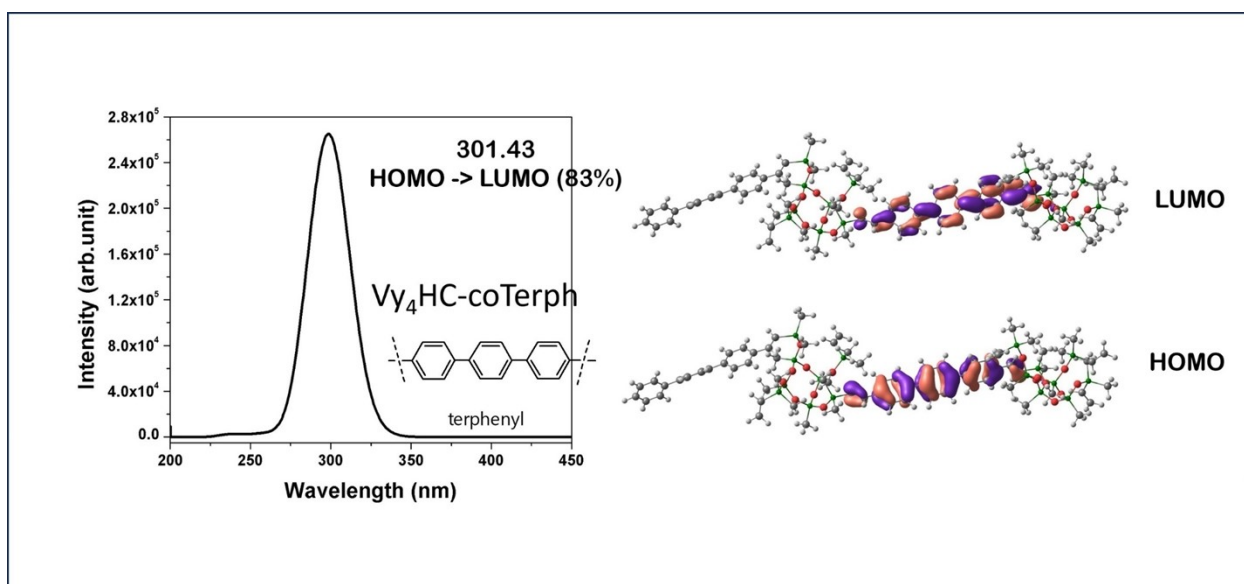


Figure S31. Calculated HOMO and LUMO and absorption spectra for the $Vy_4HC-coTerph$.

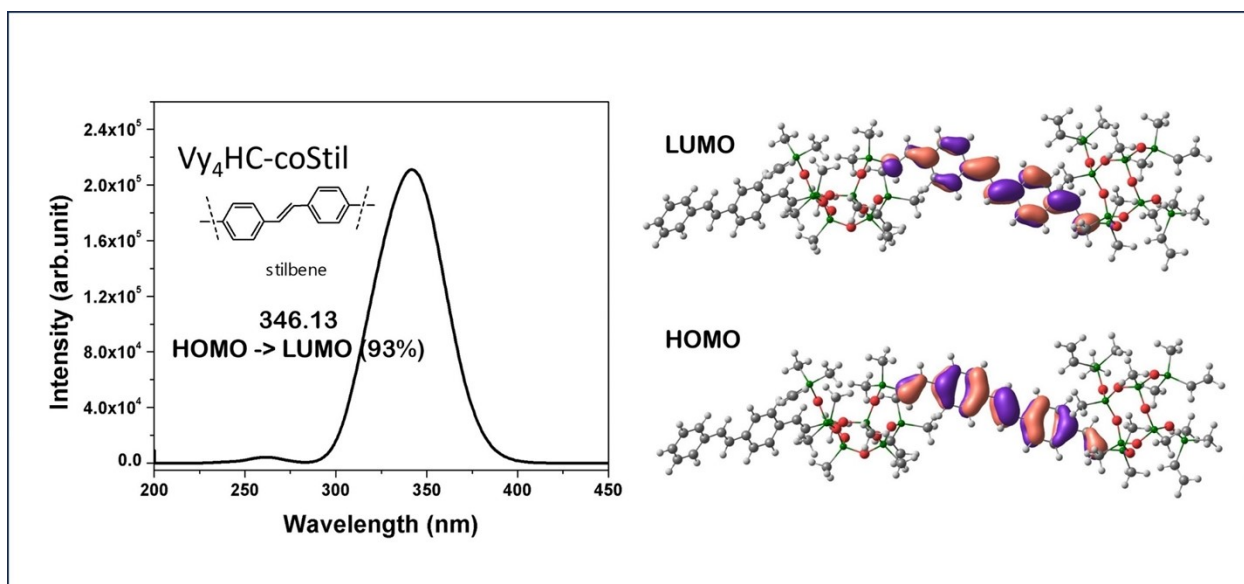


Figure S32. Calculated HOMO and LUMO and absorption spectra for the $Vy_4HC-coStil$.

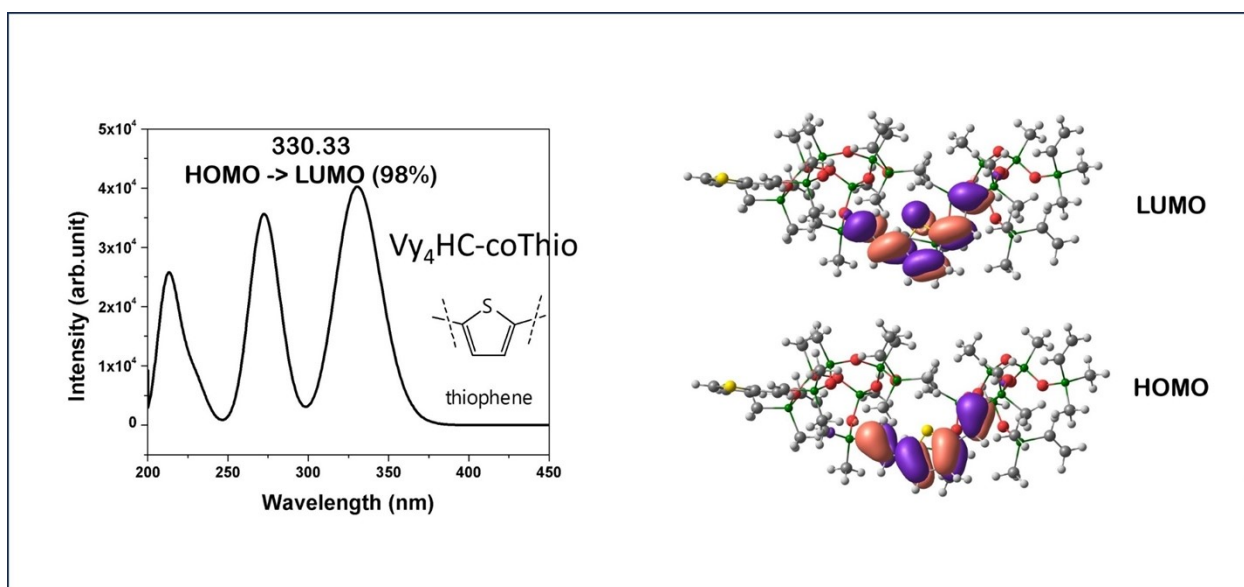


Figure S33. Calculated HOMO and LUMO and absorption spectra for the $Vy_4HC-coThio$.

References

- 1 Y. Liu, N. Takeda, A. Ouali and M. Unno, *Inorg. Chem.*, 2019, 58, 4093–4098.
- 2 C. W. Stark, M. Rammo, A. Trummal, M. Uudsemaa, J. Pahapill, M. Sildoja, S. Tshepelevitsh, I. Leito, D. C. Young, B. Szymański, O. Vakuliuk, D. T. Gryko and A. Rebane, *Angew Chem Int Ed*, 2022, 61, e202212581.