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Excited state distortions in a charge transfer state of a donor-acceptor [2]rotaxane

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Resonance Raman results

Figure S1 shows the Raman spectra of $\mathbf{R}^{4+}$ obtained at excitation wavelengths of 530.9 nm (18,836 cm^{-1}, close to the band maximum for the greatest resonance enhancement) and 647.1 nm (15,454 cm^{-1}, out of resonance with any electronic transition). Most of the intense peaks fall in the range of 500 to 1700 cm^{-1}. Spectra for $\mathbf{P}^{4+}$ were similar to those of $\mathbf{R}^{4+}$. Both components of $\mathbf{R}^{4+}$, the BHEEEN rod and the $CBPQT^{4+}$ ring, also show many Raman-active vibrational modes in the region between 500 cm^{-1} and 1700 cm^{-1}. The normal modes of $\mathbf{R}^{4+}$ and its components, obtained with 530.9 nm excitation and identical accumulation windows, are listed in Table S1. The intensities of the components are not listed as they are normal Raman intensities, showing no enhancement related to the electronic process in $\mathbf{R}^{4+}$. This can also mean that some peaks that are observed in the component spectra are not found in the [2]rotaxane spectra and vice versa, as the factors leading to the Raman intensity in each case are different. The total uncertainty in the peak positions is about ± 3 cm^{-1}, however the uncertainty between samples is only ± 0.5 cm^{-1}, making changes in peak position meaningful.

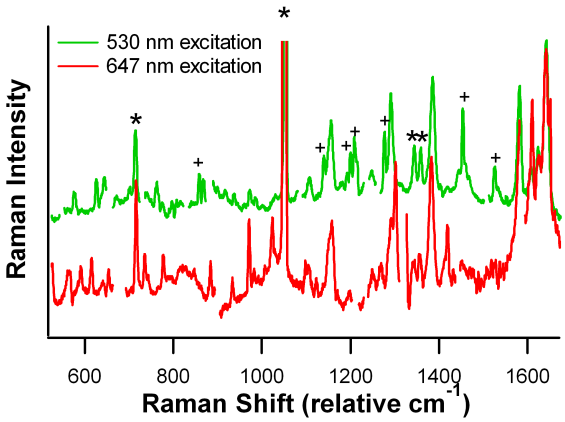

Fig. S1 The normalized resonance Raman spectra of $\mathbf{R}^{4+}$ with 530.9 nm (above) and 647.1 nm (below) excitation. The peaks marked * are the KNO_3 standard peaks. Intense laser plasma lines were subtracted out and the remaining plasma lines are marked as +.

Table S1 Full list of observed experimental Raman frequencies (cm^{-1}) for the BHEEEN and $CBPQT^{4+}$ components, and for $\mathbf{R^{4+}}$. The uncertainty in the experimental frequency between samples is ± 0.5 cm^{-1} except as noted.

BHEEEN (cm^{-1})	$CBPQT^{4+}$ (cm^{-1})	$\mathbf{R^{4+}}$ (cm^{-1})	BHEEEN (cont.)	$CBPQT^{4+}$ (cont.)	$\mathbf{R^{4+}}$ (cont.)
102		104[a]	1166		
238			1195	1195	1193
250			1219		
322			1243	1230	1248[a]
327			1259		
	400			1288	
404			1300	1301	1293
	418		1312	1312	
451				1329	
517			1357	1350	
526		524	1382		1386
535			1424		
	553		1437		
	597				1445
	637	638	1451		
		644		1459	1461
	659	660	1468		1468
	669		1471	1473	
	694			1532	1527
712			1580		1581
	732		1615	1612	1607
	742	740[a]		1635	1624
751			1649	1648	1642
		775			
813	816	814			
842	835				
901		885			
935					
951		961			
986					
1025					
1049					
1064					
1091					
		1109			
1127					
1149	1149	1157			

[a] Due to decreased experimental resolution or overlapping peaks, the error in the experimental frequencies between samples is increased to as much as ± 2 cm^{-1}.

Self absorption corrections

The calculations for the self absorption corrections follow the process laid out by Shriver and Dunn (Applied Spectroscopy, Vol 28, 1974, pp 319-323). The corrections are included in the manuscript within the error bars of the Raman profiles. The corrections come from a simplified expression,

$$\frac{\alpha_s}{\alpha_r} = \frac{I_s c_r \left(\varepsilon_s + \varepsilon_0\right)}{I_r c_s \left(\varepsilon_r + \varepsilon_0\right)}, \qquad \text{(S1)}$$

where α is the corrected effective scattering cross section, I is the integrated peak area from the resonance Raman spectrum, c is the concentration for the sample (s) and the reference (r) and ε is the extinction coefficient at the frequency of the excitation laser line (0), and the sample (s) and reference (r) scattered light. For the corrections of $\mathbf{R}^{4+}$ as a solid pellet, the extinction coefficient was ε_{max} = 780 M^{-1} cm^{-1}, as reported in reference 58, and the concentration ratio was 75.94:1 (KNO_3:$\mathbf{R}^{4+}$). In Table S2, we present the corrections for the intensity ratios of the modes observed at 530 nm excitation and used to determine the dimensionless Δ's. Only two modes (1581 cm^{-1} and 1642 cm^{-1} show a change at a level of statistical significance. In Table S3, we present the corrections for the profiles of a low (660 cm^{-1}) and high (1642 cm^{-1}) frequency mode. The correction is dependent on both the excitation wavelength and the frequency of the mode, with a maximum change of ±12%.

Table S2 Effect of self absorption correction for the normalized intensities determined at 530 nm excitation.

ω_k (cm^{-1})	I_k/I_{nit} (exp)	I_k/I_{nit} (corr)
577	0.04	0.04
640	0.05	0.05
660	0.06	0.06
885	0.04	0.04
1109	0.04	0.04
1157	0.22	0.22
1293	0.17	0.17
1386	0.27	0.27
1581	0.24	0.23
1607	0.05	0.05
1624	0.08	0.08
1642	0.43	0.42

Table S3 Effect of self absorption correction for the Raman profiles of two modes.

$\lambda_{excitation}$ (nm)	I_{660}/I_{nit} (exp)	I_{660}/I_{nit} (corr)	I_{1642}/I_{nit} (exp)	I_{1642}/I_{nit} (corr)
457.9	0.07	0.07	0.54	0.61
488.0	0.01	0.01	0.37	0.39
514.5	0.01	0.01	0.44	0.45
520.2	0.02	0.02	0.52	0.51
530.9	0.06	0.06	0.50	0.48
568.2	0.07	0.07	0.98	0.87
647.1	0.01	0.02	0.27	0.23
676.4	0.09	0.10	0.26	0.23

Raman profiles calculated with Lorentzian damping

Historically, Raman profiles calculated within the time-dependent theory of molecular spectroscopy have used a Lorentzian functional form for the damping function, $\boldsymbol{g}(t)$. Figure S2 is similar to Figure 3 in the text, only Lorentzian damping is used. The functional form of the damping used does not change the interpretation we present.

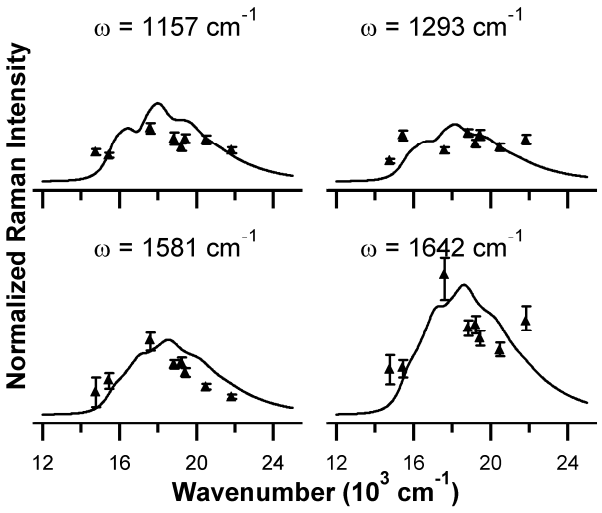

Fig. S2 Representative resonance Raman excitation profiles of four of the most enhanced normal modes of $\mathbf{R}^{4+}$. The experimental points (▲'s) are shown with experimental uncertainty bars, and the calculated fits are shown as solid lines. All experimental and calculated plots are shown on the same scale. A damping factor $\Gamma = 700$ cm^{-1} is used. The Δ's used for the calculation can be found within the text, as well as in Table S4.

Absolute distortions, in units of Ångstrøms

The Δ_k values listed in Table S4 are dimensionless distortions. These dimensionless distortions may be converted to absolute units of Ångstrøms using equation S2,

$$\delta_k = 10^8 \Delta_k \sqrt{\frac{6.023x10^{23}}{m_k} \frac{\hbar}{2\pi c \omega_k}}, \qquad \text{(S2)}$$

where δ_k is the magnitude of the coordinate change in Ångstrøms, Δ_k is the dimensionless distortion along the normal coordinate obtained from fitting the spectra, ω_k is the frequency of the observed vibrational mode in cm^{-1}, m_k is the reduced mass of the vibration in molecular mass units, $\hbar$ is Plank's constant in g cm^2 s^{-1}, and c is the speed of light in cm s^{-1}. The reduced masses are obtained from the DFT frequency calculations of the individual components. The normal modes of $\mathbf{R}^{4+}$ involve displacements of many atoms simultaneously, and the Ångstrøm values represent the change of the entire coordinate, and not of any single bond. The calculated magnitude of δ_k for each coordinate is also listed in Table S4.

Table S4 Experimental Raman frequencies, intensity ratios, distortions (dimensionless and Å) and vibrational reorganization energy contributions for the modes used in the time dependent absorption calculations of $\mathbf{R}^{4+}$. Also included are the DFT calculated frequencies and a description of the mode.

ω_k (cm^{-1})	I_k/I_{nit}	Δ_k	δ_k (Å)	λ_k	ω_{calc} (cm^{-1})	Description
577	0.04	0.67	0.069	129.85	564[a]	DNP stretch
640	0.05	0.65	0.058	130.71	650[b]	Phenylene phenyl breathing
660	0.06	0.69	0.065	157.04	665[b]	Paraquat C-C stretch
885	0.04	0.43	0.039	80.95	876[a]	DNP deformation
1109	0.04	0.35	0.034	68.99	1124[a]	DNP stretch
1157	0.22	0.75	0.065	327.89	1143[b]	Paraquat C-N stretch (outside)
1293	0.17	0.59	0.055	224.99	1355[a], 1304[b]	BHEEEN C-O stretch, Paraquat C-C stretch
1386	0.27	0.69	0.039	333.79	1420[a]	DNP C-C stretch
1581	0.24	0.57	0.031	259.81	1637[a]	DNP C-C stretch
1607	0.05	0.24	0.014	47.84	1622[b]	Phenylene C-C stretch
1624	0.08	0.32	0.019	81.57	1656[b]	Phenylene C-C stretch
1642	0.43	0.73	0.047	441.63	1678[a], 1681[b]	DNP, Paraquat C-C stretch
E_{00} (cm^{-1})	15,743					
Γ (cm^{-1})	700					

[a] Mode from BHEEEN.

[b] Mode from $CBPQT^{4+}$.

Calculated absorption spectrum of $\mathbf{P}^{4+}$

The absorption spectrum of $\mathbf{P}^{4+}$ was fit in a similar manner to $\mathbf{R}^{4+}$. Because resonance Raman profiles were not collected, they were not available to determine the Δ_k's. As with $\mathbf{R}^{4+}$, the relative distortions of the enhanced modes of $\mathbf{P}^{4+}$ were obtained from the 530.9 nm resonance Raman using Savin's formula. Because the active modes and the relative intensities are very similar to those of $\mathbf{R}^{4+}$ as shown in Table 1

of the text, the magnitudes of the Δ_k's are expected to also be similar. To fit the absorption spectrum, the Δ_k's for the nine modes showing 10% or greater intensity of the most enhanced mode (1642 cm^{-1}) used in the calculation were scaled as described in the text for $\mathbf{R}^{4+}$. The Δ_k's used to calculate the absorption spectrum of $\mathbf{P}^{4+}$ are listed in Table S5. E_{00} was determined to be 15786 cm^{-1}, and a Γ of 775 cm^{-1} was used. This fit produced a λ_v of 2535 cm^{-1} for the nine modes used in the calculation or 2910 cm^{-1} when all modes observed are considered.

Table S5 Experimental Raman frequencies, intensity ratios, distortions (dimensionless and Å) and vibrational reorganization energy contributions for the modes used in the time dependent absorption calculations of $\mathbf{P}^{4+}$.

ω_k (cm^{-1})	I_k/I_{nit}	Δ_k	δ_k (Å)	λ_k
1158	0.11	0.69	0.059	272.51
1250	0.12	0.65	0.095	260.57
1292	0.10	0.58	0.054	220.52
1384	0.27	0.89	0.049	546.84
1526	0.06	0.39	0.039	117.98
1580	0.21	0.68	0.038	370.00
1614	0.06	0.36	0.021	106.53
1623	0.03	0.26	0.016	52.97
1642	0.35	0.85	0.054	586.59
E_{00} (cm^{-1})	15,786			
Γ (cm^{-1})	775			