Electronic Supplementary Information

Enhanced detection of explosives utilizing a turn-on resonance Raman upon host-guest complexation in solution and solid state

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1. General Methods
Dichloromethane was purchased from commercial sources and purified by distillation before use. Tetrabutylammonium chloride (TBACl), 2,4-dinitrotoluene (DNT) and para-benzoquinone (BQ) were purchased from Aldrich. 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitrobenzene (TNB) were purchased from Supelco. TTF-modified calix[4]pyrrole (TTF-C[4]P) was prepared according to literature procedures. S1

Raman Spectroscopy- Raman data were recorded using a Renishaw inVia Raman microscope fitted with a diode laser (Renishaw) for 785 and an Ar + laser for 514.5 nm excitation. The instrument was interfaced with a light microscope (Leica) fitted with a 50× long working distance objective (Leica; numerical aperture 0.5) generating a 22 μm × 3 μm spot or a 50× short working distance objective (Leica; numerical aperture 0.75) with a 28 μm × 3 μm spot. The spectrometer was wavelength-calibrated using Si (520.5 cm⁻¹). Laser powers used in the experiments were adjusted to ensure sample integrity for the duration of each experiment, usually 3 mW for the 785 nm laser and 0.3 mW for the 514.5 nm laser. CH₂Cl₂ solvent bands at
703 and 1425 cm$^{-1}$ were used as internal intensity standards. No corrections for spectrometer sensitivity or self-absorption were conducted.

**UV-vis-NIR Spectroscopy**- Electronic absorption spectra were recorded using a Cary 5000 UV-vis-NIR spectrometer. For solution phase spectroscopy, quartz cuvettes were purchased from Starna Cells, Inc. UV-vis-NIR spectra were recorded from 200–1500 at 600 nm min$^{-1}$.

**UV-vis and Raman Titrations**- A 30 mM solution of the TTF-C[4]P receptor was prepared in 200 $\mu$L of CH$_2$Cl$_2$. A TNB solution (150 mM, in CH$_2$Cl$_2$) was added in aliquots from 0 to 6 equiv.. Over the course of the experiment, the total volume increased from 200 $\mu$L to 440 $\mu$L resulting in a dilution of the original solution from 30 mM to 14 mM. The same solution was used in both the Raman and UV-vis titrations. In both cases, a 1 mm path length quartz cuvette was used. After completion of this titration, TBACl (60 mM in CH$_2$Cl$_2$) was added in order to release TNB from the TTF-C[4]P host.

**Solid State Sampling**- Raman spectra of solid or crushed-up crystals of TNB$\subset$TTF-C[4]P, free TNB, and TTF-C[4]P with other nitroaromatics were collected with a 785 nm laser at 0.3 mW power or a 514 nm laser at 0.03 mW power. Spectra of the empty TTF-C[4]P receptor were not collected due to sample degradation by the laser itself, even at low power. We assume the laser-induced degradation arises from thermal effects and poor heat dissipation in the solid state. In solution, the receptor’s concentrations are lower and the solution often has better heat dissipation. Sampling of the complex in the solid state and solution did not show degradation. Intensities of the spectra were used to investigate resonance enhancement. The packing in the unit cells of the respective crystal structures show that the scatterers are aligned reasonably equally with all three axes consistent with intensities being orientationally averaged. Thus enhancements can be compared to solution phase data, which also represents orientationally averaged scattering centers.

### 2. Speciation Curve

![Speciation curve](image)

**Fig. S1** Speciation curve$^{S2}$ for the addition of TNB to TTF-C[4]P starting from an initial concentration of 30 mM and diluting to 14 mM during the addition of up to 6 equiv. of TNB in CH$_2$Cl$_2$; the binding constants used are $K_1 = 20$ M$^{-1}$ and $K_2 = 900$ M$^{-1}$ from reference.$^{S1}$

![Raman Spectra](image)

**Fig. S2** Raman spectra ($\lambda_{\text{exc}} = 785$ nm) of (a) TNB (150 mM), (b) TTF-C[4]P (30 mM) and (c) TTF-C[4]P with 6 equiv. TNB ([TTF-C[4]P] = 14 mM), in CH$_2$Cl$_2$
Fig. S3 Raman spectra ($\lambda_{exc} = 514.5$ nm) of (a) TNB (150 mM), (b) TTF-C[4]P (30 mM) and (c) TTF-C[4]P with 6 equiv. TNB ([TTF-C[4]P] = 14 mM) in CH$_2$Cl$_2$. 
Fig. S4 Raman titration data recorded with 514.5 nm excitation under identical conditions as the 785 nm Raman data in Fig. 1 of the main text: [TTF-C[4]P]$_i$ = 30 mM, black trace; TNB$^2$+TTF-C[4]P (red trace) formed upon addition of up to 6 equiv. of TNB, [TTF-C[4]P]$_f$ = 14 mM (95% complexation); CH$_2$Cl$_2$, RT. Raman intensities normalized to solvent peaks with spectral enhancement factors as defined in the main text and marked on the spectra.
**Table S1** Raman bands Assignments ($\lambda_{\text{exc}} = 785 \text{ nm}$) and spectral enhancement factors (SEFs) of the TNB$_2$·TTF-C[4]P complex.

<table>
<thead>
<tr>
<th>$\nu_{\text{TNB}}$ (cm$^{-1}$)</th>
<th>$\nu_{\text{TTF-C[4]P}}$ (cm$^{-1}$)</th>
<th>$\nu_{\text{TNB} \cdot \text{TTF-C[4]P}}$ (cm$^{-1}$)</th>
<th>SEF$^a$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>730</td>
<td>–</td>
<td>731</td>
<td>–</td>
<td>TNB</td>
</tr>
<tr>
<td>827</td>
<td>–</td>
<td>828</td>
<td>×2</td>
<td>TNB</td>
</tr>
<tr>
<td>923</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1005</td>
<td>–</td>
<td>1005</td>
<td>×6</td>
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<tr>
<td></td>
<td>1156</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>1186</td>
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<td>×10</td>
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<td>–</td>
<td>1240</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
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<td>1347</td>
<td>–</td>
<td>1342</td>
<td>×20</td>
<td>TNB</td>
</tr>
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<td>1365</td>
<td>–</td>
<td>1360</td>
<td>×14</td>
<td>TNB</td>
</tr>
<tr>
<td>1625</td>
<td>–</td>
<td>1623</td>
<td>×14</td>
<td>TNB</td>
</tr>
</tbody>
</table>

$^a$The solvent band at 703 cm$^{-1}$ was used as an internal standard to compare RRS ($\lambda_{\text{exc}} = 785 \text{ nm}$) and normal Raman ($\lambda_{\text{exc}} = 785 \text{ nm}$) spectra used to determine SEFs.

**Fig. S5** Initial linear response of TTF-C[4]P for TNB at 1360 cm$^{-1}$ band up to 0.8 equiv. (green circles) over and for TNB alone (grey squares).
Fig. S6 (a) UV−vis−NIR titration of tetrabutylammonium chloride (TBACl) into TNB$_2$⊂TTF-C[4]P (14 mM 4TTF, 6 equiv. TNB, up to 9.2 equiv. TBACl, CH$_2$Cl$_2$, RT). (b) Titration curve.

The TNB guest can be released from complexes with TTF-C[4]P to recycle the receptor by addition of chloride as evidenced by loss of the CT chromophore in UV−vis−NIR titrations (TNB; Fig. S6). Raman bands of TNB$_2$⊂TTF-C[4]P also lose intensity (see main text). The TTF-C[4]P-based bands that shifted down in energy upon complexation now shift back towards their starting frequencies, e.g., 1490 to 1492 cm$^{-1}$ and 1550 to 1554 cm$^{-1}$. Consistently, the nitro-based bands from the now free TNB also blue shift closer to frequencies observed in the uncomplexed form.

4. Computational Details

The ground state equilibrium geometries and normal modes for the TNB$_2$⊂TTF-C[4]P complex and the TNB molecule were determined using the B3LYP functional with the D2 dispersion correction$^{S3}$ (B3LYP-D2) and a 4-31G basis set using the NWChem program package.$^{S4}$ To reduce the computational cost the alkyl end chains were replaced by methyl groups. The normal Raman spectrum of TNB was calculated using a 6-31G* basis set and three-point numerical differentiation of the polarizability for each normal mode and an assumed incident laser wavelength of 514.5 nm. The differential Raman cross sections were broadened using a Lorentzian function with a full width at half max (FWHM) of 20 cm$^{-1}$.

The resonance Raman scattering (RRS) spectra were simulated using Heller’s time-dependent theory as:

$$\alpha_{\alpha\beta} = \sum_n \mu_{\alpha n}^{0n} \mu_{\beta n}^{0n} \times i \int_0^\infty \langle f | \psi_n(t) \rangle e^{i(E_L + \nu_0)Ht - \Gamma_n t} dt$$

where $E_L$ is the energy of the incident light, $n$ the electronic state, $\mu_{\alpha n}^{0n}$ the electronic transition dipole moment, $\nu_0$ the vibrational energy of state $|f\rangle$, and $|\psi_n(t)\rangle$ is the wavepacket corresponding to the time-dependent nuclear wavefunction of electronic state $n$. The homogeneous broadening is treated phenomenologically using $\Gamma_n$. The overlap between the initial and final wavepacket can be obtained analytically using the independent mode displaced harmonic oscillator (IMDHO) method. This model accounts for vibronic coupling effects but solvent effects in the calculations were not included. The simulations were done using the TDSPEC code.$^{S6}$
The dimensionless displacements needed for simulating RRS were calculated based on the B3LYP-D2 geometries and B3LYP-D2 normal modes by using a 6-31G* basis set and the LC-ωPBEh functional for calculating the excitation energies. LC-ωPBEh belong to the class of long-range corrected DFT functionals that have been shown to provide accurate excitation energies. All calculations were done using the recent implementation of long-range corrected DFT functionals into the NWChem program package. The frequencies were scaled by a factor of 1.064 to match the experimental results for the symmetric NO₂ stretch of TNB. A homogeneous broadening of 800 cm⁻¹ was used for all excited states.

Geometry Optimisation

Compared with the crystal structure (Fig. S7), the DFT geometry showed shorter hydrogen bonds between the nitro-based oxygen in TNB and the NH hydrogen of the pyrroles in the TTF-C[4]P unit with an average length of 1.8 Å from DFT compared with 2.2 Å in the crystal. The π-stacking, defined as half the distance between the central C–C bond of two TTF units, is also shortened from 3.5 Å in the crystal to 3.3 Å in the simulations. The short non-covalent bond lengths found by DFT is likely a result of the small basis set used as well as the neglect of solvent effects. In contrast, simulations that did not include the dispersion correction predicted longer non-covalent contacts with a π–π stacking of 3.7 Å and hydrogen bonds of 2.0 Å. Thus, not surprisingly the dispersion correction is important for describing the π-stacking between the TTF units and TNB, a feature of the electronic structure we expect to be important for describing the resonance condition.

Fig. S7 Comparison between crystal structure and B3LYP-D2/4-31G optimized structure of TNB₂<sub>2</sub>-TTF-C[4]P. A) Side-by-side comparison and B) overlaid structures.
Time-dependent DFT

The dominant changes in orbital occupancies for the two highest oscillator-strength transitions (Fig. S8) confirm the TTF-C[4]P→TNB CT character. On account of the CT character of the low-lying excitations, we found that it was essential to use a long-range corrected functional to obtain a reasonable description; by contrast, results based on B3LYP alone underestimate the CT excitations by more than 1 eV.

**Fig. S8** Computed changes in orbital occupancies for the $S_1$ and $S_2$ lowest energy electronic excited states of the TNB$_2$·TTF-C[4]P complex. Only the major contributions are noted; a full list of rearrangements is given in Table S1.

**Fig. S9** Molecular orbitals involved in the lowest CT excitations in TNB$_2$·TTF-C[4]P.
**Table S2** Excitation energies, oscillator strengths and compositions of the lowest CT excitations in TNB$_2$\(\subset\)TTF-C[4]P.

<table>
<thead>
<tr>
<th></th>
<th>Energy (eV)</th>
<th>Oscillator strength</th>
<th>Composition</th>
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<tbody>
<tr>
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<td>1.99</td>
<td>0.010</td>
<td>69% HOMO-A(\rightarrow)LUMO-A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13% HOMO-A(\rightarrow)LUMO-B</td>
</tr>
<tr>
<td>S2</td>
<td>1.99</td>
<td>0.010</td>
<td>64% HOMO-B(\rightarrow)LUMO-B</td>
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<td></td>
<td></td>
<td></td>
<td>18% HOMO-B(\rightarrow)LUMO-A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11% HOMO-A(\rightarrow)LUMO B</td>
</tr>
<tr>
<td>S3</td>
<td>2.01</td>
<td>0.001</td>
<td>43% HOMO-B (\rightarrow) LUMO+1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>35% HOMO-A (\rightarrow) LUMO+2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10% HOMO-B (\rightarrow) LUMO+2</td>
</tr>
<tr>
<td>S4</td>
<td>2.01</td>
<td>0.004</td>
<td>42% HOMO-A (\rightarrow) LUMO+1</td>
</tr>
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<td></td>
<td></td>
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<td>34% HOMO-B (\rightarrow) LUMO+2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11% HOMO-A (\rightarrow) LUMO+2</td>
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</tbody>
</table>

**Fig. S10** Normal modes for the C–N stretch of TNB and TNB$_2$\(\subset\)TTF-C[4]P.
Simulated Raman Spectra

Based on the electronic structure obtained using TDDFT, we simulated the RRS spectra for the complex at a wavelength coincident with the simulated excitations using the time-dependent theory of Raman scattering and the TDSPEC program (Fig. S13, green). On account of the large size of the complex, we restricted the simulations to frequencies from 1200–1500 cm\(^{-1}\). For comparison, we also simulated the normal Raman spectrum of TNB (Figure S13, blue). From the simulation, we see that the RRS spectrum is dominated by four bands situated at 1285, 1336, 1349 and 1372 cm\(^{-1}\). Overall, we see fair agreement with the experimental results, particularly in the prediction of greater resonance enhancement for the mode around 1340 cm\(^{-1}\) and the 10-fold enhancement in the mode around 1365 cm\(^{-1}\). The mode at 1285 cm\(^{-1}\) corresponds to the C–N stretch of TNB, which we correlate to the 1256 cm\(^{-1}\) mode seen in RRS of the solid-state spectrum of the complex. In solution, this mode overlaps with a solvent band and cannot be resolved. The modes at 1336 and 1349 cm\(^{-1}\) correspond to –NO\(_2\) stretches of TNB and are degenerate in the free TNB molecule. For the free TNB molecule, this band is very weak and
consequently it experiences a strong resonance enhancement in the complex. Experimentally, only a single broad band is observed at 1342 cm\(^{-1}\). While it is possible that two modes are contributing to the band, the separation found in the simulations may result from an overestimation of the binding of TNB within the calculated structure, leading to a greater separation of the band. The band at 1372 cm\(^{-1}\) corresponds to the symmetric \(-\text{NO}_2\) stretch of TNB. Thus, all modes found strongly modulate the TNB-based LUMO orbitals involved in the lowest-energy CT excitations explaining their resonance enhancements.

Interestingly, TDDFT simulations using the structure with longer \(\pi-\pi\) and hydrogen bond contacts obtained without the dispersion corrections leads to very similar excitation energies but the oscillator strengths were significantly smaller resulting in no resonance enhancements. In a related study, we were able to neglect these dispersion effects when computing the geometry of the electron donor-acceptor complex involving tetrathiafulvalene. In that case, the rigid box-shaped cyclobis(paraquat-p-phenylene) receptor was employed. Its \(\sim 3.5\) Å size creates a perfect \(\pi\)-stacking cavity that enforces short contacts. For the TTF-C[4]P receptor examined here, however, its less rigid and hinged calix[4]pyrrole core means that the inclusion of dispersion effects is critical for describing the geometry and electronic character of the complex.

![Simulated resonance Raman spectrum using 620 nm excitation](image)

**Fig. S13** Simulated resonance Raman spectrum using 620 nm excitation for (a) TNB\(_2\)⊂TTF-C[4]P and (b) normal Raman spectrum of TNB. Frequencies have been multiplied by 1.064 to match the experimental results for the symmetric \(-\text{NO}_2\) stretch of TNB.
5. Solid State Spectra of Nitroaromatics TNT, DNT and BQ and their Complexes

Fig. S14 Solid state Raman spectra of (a) TNT ($\lambda_{exc} = 785$ nm), (b) TTF-C[4]P ($\lambda_{exc} = 785$ nm), (c) TNT$_2$<sub>c</sub>TTF-C[4]P ($\lambda_{exc} = 785$ nm), (d) TNT$_2$<sub>c</sub>TTF-C[4]P ($\lambda_{exc} = 514$ nm) and (e) TNT ($\lambda_{exc} = 514$ nm).
Fig. S15 Solid state Raman spectra of (a) TNB ($\lambda_{\text{exc}} = 785$ nm), (b) TTF-C[4]P ($\lambda_{\text{exc}} = 785$ nm), (c) TNB$_2$$\subset$TTF-C[4]P ($\lambda_{\text{exc}} = 785$ nm), (d) TNB$_2$$\subset$TTF-C[4]P ($\lambda_{\text{exc}} = 514$ nm) and (e) TNB ($\lambda_{\text{exc}} = 514$ nm).
Fig. S16 Solid state Raman spectra of (a) DNT ($\lambda_{\text{exc}} = 785$ nm), (b) TTF-C[4]P ($\lambda_{\text{exc}} = 785$ nm), (c) DNT$_2\subset$TTF-C[4]P ($\lambda_{\text{exc}} = 785$ nm), (d) DNT$_2\subset$TTF-C[4]P ($\lambda_{\text{exc}} = 514$ nm) and (e) DNT ($\lambda_{\text{exc}} = 514$ nm).
Fig. S17 Solid state Raman spectra of (a) BQ ($\lambda_{exc} = 785$ nm), (b) TTF-C[4]P ($\lambda_{exc} = 785$ nm),
(c) BQ$_2$⊂TTF-C[4]P ($\lambda_{exc} = 785$ nm), (d) BQ$_2$⊂TTF-C[4]P ($\lambda_{exc} = 514$ nm) and (e) BQ ($\lambda_{exc} = 514$ nm).
Fig. S18 Solid state Raman spectra ($\lambda_{exc} = 514$ nm) of (a) $\text{TNT}_2\subset\text{TTF-C}[4]\text{P}$, (b) $\text{TNB}_2\subset\text{TTF-C}[4]\text{P}$, (c) $\text{DNT}_2\subset\text{TTF-C}[4]\text{P}$ and (d) $\text{BQ}_2\subset\text{TTF-C}[4]\text{P}$. 
**Fig. S19.** Comparisons of Raman spectra ($\lambda_{\text{exc}} = 785$ nm) of solids of TTF-C[4]P complexes with TNT (blue), TNB (purple), DNT (green) and BQ (red). Colored boxes are used to assign vibrations as TTF-C[4]P (yellow), nitroaromatic (red) or as BQ (blue) based.

**Fig. S20** Comparisons of Raman spectra ($\lambda_{\text{exc}} = 514.5$ nm) of solids of TTF-C[4]P complexes with TNT (blue), TNB (purple), DNT (green) and BQ (red). Colored boxes assigned in Fig. S19.
6. References


