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# Raman spectroscopy of dipyrrins: nonresonant, resonant and surface-enhanced cross-sections and enhancement factors

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Detailed studies of the mechanism of surface-enhanced (resonance) Raman spectroscopy (SE(R)RS), and its applications, place a number of demands on the properties of SERS scatterers. With large Raman cross-sections, versatile synthetic chemistry and complete lack of fluorescence, free dipyrrins meet these demands but the Raman and SE(R)RS spectroscopy of free dipyrrins is largely unknown. The first study of the Raman spectroscopy of free dipyrrins is therefore presented in this work. The nonresonant Raman, resonant Raman and surface-enhanced Raman spectra of a typical *meso* aryl-substituted-dipyrrin are reported. Absolute differential cross-sections are obtained for excitation wavelengths in the near infrared and visible region, in solution phase and for dipyrrin adsorbed on the surface of silver nanoparticles. Raman enhancement factors for SERRS and resonance Raman are calculated from the observed differential cross-sections. The magnitudes of the resonantly enhanced cross-sections are similar to those recently reported for strong SERS dyes such as Rhodamine 6G and Crystal Violet. Free dipyrrins offer the advantages of existing SERS dyes but without the drawback of strong fluorescence. Free dipyrrins should therefore find applications in all areas of Raman spectroscopy including fundamental studies of the mechanisms of SERS and bioanalytical and environmental applications. Copyright © 2011 John Wiley & Sons, Ltd.

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Keywords: dipyrrin; resonance Raman spectroscopy; SERS; Raman cross-sections; Raman enhancement factors

## Introduction

Dipyrrins are bispyrrolic compounds first reported by Fischer and Orth in 1937.<sup>[1]</sup> Dipyrrin research has attracted considerable interest over many years and is currently experiencing a renaissance.<sup>[2,3]</sup> The conjugated  $\pi$  system of the free dipyrrin unit, analogous to porphyrins, provides free dipyrrins and their metallo complexes with interesting and useful optical properties. Free dipyrrins and their complexes display promise as light harvesters,<sup>[4-7]</sup> sensitizers for solar cells,<sup>[4]</sup> and as components of chromophores in metal organic frameworks<sup>[5,6]</sup> and molecular materials.<sup>[7]</sup> Dipyrrins also display versatile structural properties and various functional groups may be incorporated into the dipyrrin unit by substitution on the aryl and/or pyrrole rings.<sup>[2,8]</sup> Because of strongly allowed  $\pi - \pi^*$  transitions, free dipyrrins have large transition dipole strengths (absorption coefficients of 20  $000 \text{ M}^{-1} \text{ cm}^{-1}$  and oscillator strengths of 0.5), which make them ideal candidates for resonantly enhanced Raman spectroscopies that rely on enhancement through coupling to dipole-allowed electronic transitions such as resonant Raman and surface-enhanced Raman scattering (SERS). Surprisingly, there are no publications involving the Raman spectroscopy of free dipyrrins. The SERS spectra of dipyrrin–BF<sub>2</sub> complexes have been reported and the only reported Raman cross-sections for dipyrrin compounds are for the recently reported ruthenium complex.<sup>[9]</sup> Boron complexes of dipyrrins are widely known for their excellent emission properties and the success of BODIPY<sup>™</sup> complexes in fluorescence applications in particular, may have obscured the promising Raman properties of the free dipyrrin unit.

For the development of reliable SERS applications, the Raman cross-sections and enhancement factors must be known. Since the first report of SERS from single molecules,<sup>[10,11]</sup> there has been much debate on the magnitude of SERS enhancement factors. As demonstrated by Le Ru et al. there are a large number of factors that contribute to the SERS effect. Putting aside the issue of hotspot formation and number of molecules in the scattering volume, in surface-enhanced resonance Raman scattering (SERRS) it is important to take into account both enhancement from resonance with the electronic states of the molecule (the resonance Raman effect) and enhancement from resonance with the plasmon modes of the metallic nanostructure (the SERS effect). A further complication is the presence of resonant enhancement via electronic transitions between the molecule and metal states. The vast majority of single-molecule SERS (SM-SERS) experiments are performed under SERRS conditions. The molecular electronic resonance is clearly a major factor in the extremely large Raman cross-sections observed in SM-SERS experiments, but unfortunately,

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the best-performing SM-SERS scatterers (e.g. Rhodamine 6G (R6G), Crystal Violet, boron-dipyrromethene dyes) have excellent fluorescence quantum yields, which largely precludes the measurement of the resonance Raman cross-sections in solution. Recently, femtosecond stimulated Raman spectroscopy (FSRS),<sup>[12]</sup> and the SERS effect itself<sup>[13]</sup> have been used to estimate resonant Raman cross-sections of R6G in solution. Although FSRS provides accurate values, it is technically very demanding while using the SERS effect carries a number of caveats. An advantage of using free dipyrrins for SERS measurements is the complete absence of fluorescence, which allows the resonance Raman cross-sections to be measured simply and accurately, which in turn allows a more accurate assessment of the enhancement mechanisms in SERS.

Until recently the concept of enhancement factor was not well defined and as a result SERS enhancement factors reported in the literature covered a wide range, from 10<sup>4</sup>-10<sup>14</sup> SERS enhancement factors depend largely on the precise conditions of the SERS experiment: the substrate (metal surface - gold/silver, nanoparticles (size)/roughed surface), excitation wavelength (proximity to plasmon resonance or analyte resonance), detection setup (scattering geometry - 135/180° degree backscattering), properties of the analyte, SERS analyte adsorption properties (surface coverage, distance from surface, adsorption orientation), etc.<sup>[14,15]</sup> Similarly, the physical mechanisms responsible for the enhancement seen in SERS were subject to much debate. Recently, Lombardi and Birke<sup>[16,17]</sup> have provided a theoretical description of surface-enhanced Raman using Albrecht's approach<sup>[18]</sup> for resonantly enhanced Raman scattering. Lombardi and Birke note that in addition to the familiar A-term scattering observed in molecular resonant Raman spectra, the less common B-term and C-term resonances can also make substantial contributions to the enhancements observed in SERS (and SERRS) experiments via charge-transfer transitions between the molecule and metal nanoparticle.

In this work, we measure the nonresonant, resonant, and surface-enhanced Raman cross-sections and calculate the enhancement factors of a simple dipyrrin system (Scheme 1) following the recent definition given by Le Ru *et al.*<sup>[15]</sup> We present assignments of the vibrational modes of dipyrrins using density functional theory (DFT) calculations of the nonresonant Raman spectra. We use these assignments, along with time-dependent DFT calculations to explain the enhancements observed in the resonant Raman spectra of dipyrrins on silver nanoparticles within the unified picture of SERS as presented by Lombardi and Birke.



**Scheme 1.** 5-(4-Methoxycarbonylphenyl)-4,6-dipyrrin, **1**.

## **Computational and Experimental Procedures**

#### **Computational methods**

All calculations were performed using GAUSSIAN09.<sup>[19]</sup> DFT was used, with the Becke's three-parameter exchange functional (B3)<sup>[20]</sup> in combination with the correlation functional of Lee, Yang and Parr (LYP);<sup>[21]</sup> O3LYP,<sup>[22]</sup> which has essentially the same form as B3LYP but the OPTX<sup>[23]</sup> density functional replaces the Becke parameter; and a new hybrid exchange correlation functional M06.<sup>[24]</sup> 6-311 (+)G(2d,2p) basis sets were used for all optimisation and Raman wavenumber calculations. Self-consistent reaction field methods, more specifically the polarisable continuum model (CPCM) of Cossi et al.<sup>[25]</sup> were used to model solvent effects. All geometry optimizations, wavenumber, and time-dependent calculations were carried out using the CPCM model. A comparison of the B3LYP, O3LYP and M06 functionals was carried out using mean average deviation between the experimental Raman wavenumbers and the calculated Raman wavenumbers (Fig. S1, Table S1) and a comparison of the experimental and calculated absorption spectra (Fig. S2, Table S2). From these evaluations the B3LYP functional gave the closest agreement between calculated and experimental parameters. GAUSSSUM 2.2.4<sup>[26]</sup> was used to extract vibrational wavenumbers and Raman activities from the calculations. The calculated Raman spectrum is a convolution of a series of  $\delta$ -functions, scaled by the calculated intensities and located at the calculated wavenumbers, and a Gaussian function with full width at half maximum (FWHM) of 5 cm<sup>-1</sup>. Raman wavenumbers were scaled using literature values for each functional and basis set.<sup>[27-29]</sup> The results of the above calculations were used to analyse and identify the vibrational wavenumbers, normal modes, and Raman activities. Calculations for the electronic excited states were performed using the time-dependent DFT (TD-DFT) calculations with the B3LYP/6-311(+)G(2d,2p) model. The calculated absorption spectrum is a convolution of a series of  $\delta$ -functions, located at the transition wavenumber and scaled by the calculated oscillator strengths, and a Gaussian with a FWHM value determined from the FWHM values of the corresponding peaks of the experimental absorption spectrum.

## **Experimental Procedures**

### Preparation of dipyrrin ligand: 1

**1** was prepared following literature procedures.<sup>[30,31]</sup> Briefly, the appropriate aldehyde was condensed with pyrrole via an HCl catalyzed condensation at room temperature, which was followed by oxidation of the resulting dipyrromethane with DDQ. Purification was achieved via column chromatography on deactivated alumina using  $CH_2Cl_2$  as the eluent.

#### Preparation of silver nanoparticles

Silver nanoparticles were prepared via the trisodium citrate reduction of silver nitrate method of Lee and Meisel.<sup>[32]</sup> A 1-mM stock solution of silver nitrate and 34 mM solution of trisodium citrate were prepared in Milli-Q water. Five millilitres of the silver nitrate stock solution was heated to approximately 90 °C and 0.1 mL of trisodium citrate was added and the solutions were heated in a hot water bath for 1 h.

#### Preparation of samples for SERS

The conditions required for single molecule SERS of R6G on silver nanoparticles were used, as reported by Le Ru *et al.*<sup>[33]</sup> Briefly, a 40 mM solution of KCl was prepared in Milli-Q water. Of the KCl stock solution, 0.25 mL was added to a 0.5 mL volume of freshly prepared silver nanoparticles, followed by 0.25 mL of  $2.0 \times 10^{-6}$  M solution of dipyrrin in water, giving a final concentration of 10 mM KCl and  $5.0 \times 10^{-7}$  M dipyrrin. This procedure consistently produces large SERS intensities for the cationic R6G (sufficient for single-molecule SERS) but we have not attempted to adjust these conditions to optimize the SERS enhancement of dipyrrins.

## **Raman Spectroscopy**

Nonresonant Raman spectra (1064 nm) were collected on powder samples and solutions in methanol (11.2 mM) using a Bruker IFS-55 FT-interferometer bench equipped with an FRA/106 Raman accessory and using OPUS (version 4.0) software. A Nd:YAG laser with 1064 nm excitation wavelength was used. An InGaAs diode (D424) operating at room temperature was used to detect Raman photons. Spectra were typically measured using 256 scans at a power of 90 mW and a resolution of 4 cm<sup>-1</sup>.

Resonance Raman and SERS spectra were collected using either a Crystallaser (444.2 nm excitation) or a ModuLaser Stellar-Pro argon laser (457.9 and 488.0 nm excitation) and spectra were collected using a system previously described.<sup>[34-37]</sup> Excitation power ranged from 6-20 mW at the sample. Solutions for resonance Raman were prepared in dichloromethane (0.461 mM). Raman and Rayleigh scattering light was collected from the sample cell using either 180° backscattering geometry or 135° back-scattering geometry. Rayleigh scattering was rejected using Raman edge filters from Iridian Technologies or notch filters from Kaiser Optical Systems. The scattered photons were focused onto the entrance slit of an Acton Research SpectraPro<sup>®</sup> 2550i, 0.500 m imaging single stage monochromator/spectrograph and detected with a Roper Scientific Spec-10:100B CCD detector controlled by WINSPEC software. A combination of cyclohexane and a 50/50 v/v mix of toluene and acetonitrile (ASTM E 1840 Raman Shift Standard) were used for the wavenumber calibration. Wavenumber calibration was accurate to 0.5–1 cm<sup>-1</sup>. Resolution ranged from 2-4 cm<sup>-1</sup> depending on spectral position. Peak positions were reproducible to within  $1 \text{ cm}^{-1}$ .

## **Raman Cross-sections**

For nonresonant Raman cross-section measurements in methanol solution, solute absolute differential Raman cross-sections were obtained relative to solvent cross-sections by

$$\left(\frac{d\sigma_{\text{RS}}}{d\Omega}\right)_{\text{sample}} = \left(\frac{d\sigma_{\text{RS}}}{d\Omega}\right)_{\text{reference}} \cdot \frac{I_{\text{sample}}}{I_{\text{reference}}} \cdot \frac{c_{\text{reference}}}{c_{\text{sample}}}$$
(1)

using the solvent (methanol) as an internal standard. The differential cross-section of the 1035 cm<sup>-1</sup> band of methanol at 1064 nm ( $7.8 \times 10^{-32}$  cm<sup>2</sup> sr<sup>-1</sup>) is obtained from the A-Term parameters reported by Moran *et al.*<sup>[38]</sup> Colles and Griffith<sup>[39]</sup> reported an absolute differential cross-section for the 1035 cm<sup>-1</sup> band of methanol with 488 nm excitation of  $2.5 \times 10^{-30}$  cm<sup>2</sup> sr<sup>-1</sup> (Moran and Kelley's parameters give  $2.3 \times 10^{-30}$  cm<sup>2</sup> sr<sup>-1</sup> with 488 nm excitation). Le Ru *et al.* showed that the nonresonant Raman cross-sections of 2-bromo-2-methylpropane (2B2MP) can be accurately calculated using density functional techniques.<sup>[15]</sup> A B3LYP/6-311(+)G(2d,2p) calculation (with the CPCM solvent model) of methanol gives a value of  $6.9 \times 10^{-32}$  cm<sup>2</sup> sr<sup>-1</sup> for 1064 nm excitation for the 1035 cm<sup>-1</sup> band, in very close agreement with the value of Moran *et al.*, and we use  $7.8 \times 10^{-32}$  cm<sup>2</sup> sr<sup>-1</sup> in this work. The cross-sections obtained by Moran and Kelley and the data reported here were obtained using similar back-scattering geometries. Dichloromethane was used as an internal standard for measurements of resonant Raman cross-sections. The absolute differential Raman cross-section of sodium sulfate in water (concentration = 0.100 M) was used as an external standard for the calculation of the SERS cross-sections.<sup>[41]</sup>

## **Results and Discussion**

#### Absorption spectrum and TD-DFT calculations

The optimised structure of **1** with the atom labels used for mode assignment is displayed in Fig. 1. The pyrrolic rings are planar while the phenyl ring makes a torsion angle of  $66^{\circ}$  with the pyrrolic rings. As predicted by Brückner *et al.* <sup>[42]</sup> this reduces the steric interactions between the hydrogen atoms (H<sub>25</sub>, H<sub>11</sub>; H<sub>6</sub>, H<sub>18</sub>).

The position and intensity of the electronic resonance of the molecule plays a key role in determining the enhancement in both resonant Raman<sup>[43]</sup> and SERS.<sup>[16,17,44–47]</sup> The experimental and calculated absorption spectra of **1** in methanol is given in Fig. 2. The TD-DFT calculations show several configurations that contribute to the electronic transitions of **1** (Table 1, Fig. S3). The broad dominant transition at 432 nm is assigned as a  $\pi$ - $\pi$ \* transition based on the results of the TD-DFT calculation, which predicts the transition at 408 nm. There are two higher energy transitions at 300 nm and 231 nm. The calculation predicts a transition at 339 nm, two closely spaced transitions at 311 and 313 nm, and 248 nm, which can all be assigned as  $\pi$ - $\pi$ \* type transitions.

The electron density difference maps for the strongest transitions are shown in Fig. 3. These maps plot regions of charge-density depletion (light) and accumulation (dark) between the ground and excited-states. They are a useful guide to interpreting the resonant Raman spectra, as vibrational modes located in regions of large charge-density changes should receive the greatest resonant enhancement. Clearly they are all  $\pi - \pi^*$  type transitions.



**Figure 1.** Optimised structure of **1** (DFT/B3LYP 6-311 + G (2d, 2p)) with atom labels adopted for mode assignments.

## RAMAN SPECTROSCOPY

Despite the nonplanarity of the phenyl ring there is also significant movement of charge-density onto the phenyl ring during the  $\pi-\pi^*$  transition. Similar changes in charge-density over the phenyl ring have been proposed to explain the enhanced transannular torsional mode intensity in the resonant Raman spectra of the ruthenium complexes of dipyrrin ligands.<sup>[9,31]</sup>

It is worth noting that strong exciton coupling is observed in metallodipyrrin complexes with multiple dipyrrin ligands.<sup>[48]</sup> This may be relevant for SERS studies (see below) as the free dipyrrins adsorbed on a nanoparticle may be in sufficiently close proximity for strong electronic interactions and exciton coupling. Similar effects have been observed with other dyes that are known to exhibit exciton coupling, e.g. dimer formation in R6G.<sup>[46]</sup>

#### Nonresonant cross-sections

The calculated and experimental nonresonant Raman spectra of **1** are shown in Fig. 4. The calculated wavenumbers have been scaled by 0.9679. This scaling factor is recommended for the B3LYP/6–311 + G (d,p) basis sets and larger.<sup>[49]</sup>

The differential cross-sections were determined from the calculated Raman scattering activities ( $R_i$ )<sup>[50–54]</sup> using Eqn (2), where the differential cross-section for a vibrational mode with wavenumber  $\bar{v}_i$  can be expressed as<sup>[55]</sup>



**Figure 2.** Absorption spectra of **1** in methanol. (A) Experimental and (B) simulated line shape using calculated oscillator strengths obtained from DFT calculations.

where *C* is a constant  $(C = \pi^2/45\varepsilon_o^2)$  and  $\varepsilon_o \equiv$  permittivity of free space = 8.8542 × 10<sup>-12</sup> F m<sup>-1</sup>,  $B_i^2 = (h/8\pi^2 c \bar{v}_i) [\text{kg m}^2]$  is the square of the zero point amplitude for the normal mode in reduced mass coordinates,  $\bar{v}_R$  is the wavenumber of the Stokesshifted Raman signal and  $R_i [\varepsilon_o^2 m^4 \text{kg}^{-1}]$  is the Raman scattering activity from Gaussian output.<sup>[15]</sup>  $K(T) = [1 - \exp(-hc\bar{v}_i/kT)]^{-1}$ accounts for the thermal population of the vibrational state. Equation (2) gives the Raman cross-section in the gas phase. To obtain the predicted liquid phase cross-section a local field correction factor, *L*, is applied where  $L = [(n^2 + 2)/3]^4$  and *n* is the refractive index of the solvent.

The experimental nonresonant Raman intensities (in methanol with 1064 nm excitation) are obtained using the solvent line at 1035 cm<sup>-1</sup> as an intensity standard. Only the five strongest dipyrrin modes ( $q_{66}$ ,  $q_{69}$ ,  $q_{71/}q_{72}$ ,  $q_{82/83}$ ,  $q_{84}$ ) are observed. The Raman cross-sections for these modes are given in Table 2 and Fig. 5 shows the Cartesian displacement vectors for these modes. The nonresonant Raman spectrum obtained as a KBr pellet (Fig. 4(b)) displays several



**Figure 3.** Electron density difference plots for the strongest transitions of **1**. Light represents depletion of electron density and dark represents accumulation of electron density.

Experime	ental		Calculated	
$\lambda$ / nm	$\epsilon$ / L mol <sup>-1</sup> cm <sup>-1</sup>	λ / nm	Configuration (% contribution)	Oscillator strength
432	18 900	408	$HOMO^a \rightarrow LUMO^b$ (95)	0.536
		339	$HOMO \rightarrow LUMO + 1$ (95)	0.105
300	8 200	313	HOMO-3 $\rightarrow$ LUMO (97)	0.162
		311	HOMO-5 $\rightarrow$ LUMO (-23), HOMO-2 $\rightarrow$ LUMO (71)	0.054
231	15 600	248	HOMO-7 $\rightarrow$ LUMO (50), HOMO-3 $\rightarrow$ LUMO + 1 (-32), HOMO-2 $\rightarrow$ LUMO + 1 (-11)	0.365
<sup>a</sup> HOMO, <sup>b</sup> LUMO, I	highest occupied mo	olecular orb nolecular or	ital. bital.	



**Figure 4.** Calculated and experimental Raman spectrum of **1** with some normal modes highlighted. (A) Calculated spectrum using DFT/B3LYP 6-311 + G (2d,2p). Wavenumbers are scaled by 0.9679.<sup>[[49]]</sup> (B) Solid-state nonresonant Raman spectrum as a KBr pellet. (C) Solution phase nonresonant Raman spectrum in methanol (S = methanol peaks).

other Raman active modes. We obtain nonresonant cross-sections for the observed bands in Fig. 4(b) by assuming the band at 1576 cm<sup>-1</sup> has the same cross-section in the solution and solid phases (a reasonable approximation given the experimental error associated with the cross-section measurements). Using a dipyrrin mode as its own internal standard avoids issues with polarization and concentration when dealing with solid samples. Table 2 displays the calculated and experimental nonresonant Raman cross-sections for 1, mode assignments and mode descriptions as the percentage contribution of redundant internal coordinates to each of the normal mode. The calculated and experimental values show excellent agreement which provides confidence in the veracity of the electronic structure calculations. As expected, modes associated with the dipyrrin core dominate the nonresonant Raman spectrum with some contribution of modes from the phenyl group.

#### Resonance Raman, resonance cross-sections and enhancement factors

The resonant Raman excitation wavelengths (444.2 nm, 457.9 nm, 488.0 nm) are strongly resonant with the  $\pi$ - $\pi$ \* transition and also on the red edge of the electronic transition of interest, which avoids any complication of preresonance enhancement from the higher energy transitions. As can be seen from Fig. 6 most features that are in the nonresonant Raman spectrum are also common to all the resonant Raman spectra.

Table 3 gives the resonant Raman cross-sections and resonant Raman enhancement factors for **1**, for 444.2 nm, 457.9 and 488.0 nm excitation. At 444.2 nm the resonant Raman cross-sections are on the order of  $10^3$ – $10^5$  times larger than the nonresonant Raman cross-sections, consistent with resonance with a strongly allowed  $\pi$ – $\pi$ \* transition. As the laser excitation moves away from the centre of the electronic transition (at 432 nm), the resonant Raman cross-sections decrease by at least an order of magnitude. Despite their importance in studies of SERS, with only two notable exceptions,<sup>[12,13]</sup> there are no reports of resonant Raman enhancement factors for commonly used dyes in SERS experiments, first

because the nonresonant cross-sections are not typically measured and the most common SERS dyes have very strong fluorescence cross-sections that preclude measurement of resonance Raman spectra. There are several reports of resonant cross-sections for strongly enhanced Raman scatterers with visible excitation such as betaine-30 (maximum cross-section  $1.6 \times 10^{-25}$  cm<sup>2</sup> sr<sup>-1</sup>),<sup>[56]</sup> the nonlinear chromophore julolidinyl-n-N,N'-diethylthiobarbituric acid (JTB) with a maximum cross-section of  $7 \times 10^{-24}$  cm<sup>2</sup> sr<sup>-1</sup>,<sup>[38]</sup> the azo dye Disperse Red (a maximum *total* cross-section of  $6.0 \times 10^{-25}$  cm<sup>2</sup>),<sup>[57]</sup> and  $[Ru(bpy)_3]^{2+}$  (1.0 × 10<sup>-24</sup> cm<sup>2</sup> sr<sup>-1</sup>),<sup>[58]</sup> which are similar in magnitude to the values reported here for the free dipyrrin systems. The cross-sections reported here are also in good agreement with the cross-sections for the ruthenium complex of a meso-aryl-substituted-dipyrrin  $(1.6 \times 10^{-24} \text{ cm}^2 \text{ sr}^{-1} \text{ for the } 409 \text{ cm}^{-1} \text{ band})$ .<sup>[9]</sup> Resonant Raman cross-sections for fluorescent dyes, R6G (1510 cm<sup>-1</sup> band,  $1.5 \times 10^{-24}$  cm<sup>2</sup> sr<sup>-1</sup> with 532 nm excitation), and Crystal Violet (1650 cm<sup>-1</sup> band,  $6.7 \times 10^{-25}$  cm<sup>2</sup> sr<sup>-1</sup> with 568 nm excitation) commonly used in SM-SERS have been estimated by using the SERS effect to quench spontaneous emission.<sup>[13]</sup> FSRS gives a value of  $1.5\times10^{-24}\,\text{cm}^2\,\text{sr}^{-1}$  for the 1510  $\text{cm}^{-1}$  band of R6G with 532 nm excitation.<sup>[12]</sup> This suggests that dipyrrins have the requisite electronic enhancement to be candidates for single-molecule SERS investigations. The ability to obtain a complete characterization of nonresonant Raman, resonant Raman and SERS is a very attractive feature of dipyrrin dyes.

The strongest modes in the resonance Raman spectra are mode 82+83 and mode 69. Electronic structure calculations (TD-DFT) show that during the  $\pi - \pi^*$  transition substantial electron density changes occur in the pyrrole rings and over the phenyl ring. Mode 83 is a phenyl ring deformation and mode 69 and 82 are pyrrole ring deformations. Therefore, the strong enhancement of these modes is consistent with the changes in electron density predicted by the TD-DFT calculations. The low symmetry of the dipyrrin systems and the extensive delocalization of the electron density changes provide an explanation for the enhancement of nearly all the vibrational modes. Consequently, all enhanced modes are enhanced via A-term scattering (therefore the ground and excited  $\pi - \pi^*$  state are Frank–Condon coupled). Under Franck– Condon coupling, the oscillator strength of the electronic transition and the mode displacements between the ground and excited states determine the mode intensities. The large intensity of mode 83 implies substantial structural reorganization of the phenyl ring in the  $\pi - \pi^*$  excited state. As shown in dipyrrin complexes<sup>[9]</sup> the structural reorganization of the phenyl ring is mostly associated with rotation of the ring about the transannular bond. It is appropriate to make some comparison between the electronic structures and resonant Raman features of phenyl-substituted dipyrrins and tetraphenylporphyrin species. In contrast to the strong enhancement of the phenyl modes in the dipyrrin spectra reported here, phenyl modes in tetraphenylporphyrin are only weakly enhanced via resonance with the strongly allowed Soret bands (A-term enhancement), and the enhancement is typically ascribed to intensity borrowing from nearby pyrrole modes.<sup>[59]</sup> Weak electronic conjugation between the phenyl ring and the porphine  $\pi$ -system and poor coupling between the phenyl and pyrrole vibrational modes are the causes of the weak enhancement. However, in the dipyrrin system the strong enhancement of the phenyl modes and the @electronic structure calculations both indicate that the phenyl and pyrrole  $\pi$ -systems interact strongly. This may be due to the conformational flexibility of the free dipyrrin unit that allows orbital overlap between the phenyl substituent and the dipyrrin core. Therefore, substituents on the phenyl ring should have a strong

ons for 1	Mode assignments <sup>e</sup>		$q_{36} = 0.030  d_{22,21,26,30}$	$q_{42} = - \ 0.037 \ d_{8,16,17,18} + 0.044 \ d_{8,16,24,25} + 0.035 \ d_{20,19,21,26} - 0.039 \ d_{26,21,22,23} - 0.036 \ d_{20,19,21,26} - 0.039 \ d_{26,21,22,23} - 0.036 \ d_{26,21,22} - 0.$	$0.036  d_{21,22,24,25} + 0.033  d_{23,22,24,16}$	$q_{44} = -0.034r_{0.10} - 0.050r_{0.28} + 0.030a_{12.13}$	$q_{49} = 0.056  d_{8,16,17,18} + 0.036  d_{24,16,17,18} = 0.030  d_{16,17,19,20} = 0.088  d_{18,17,19,20} = 0.0000  d_{18,17,19,20} = 0.00000  d_{18,17,19,20} = 0.0000000000  d_{18,17,19,20} = 0.000000000000000000000000000000000$	$\begin{array}{l} 0.035  d_{18,17,19,21} + 0.035  d_{20,19,21,22} \\ q_{51} = 0.101 r_{12,14} + 0.032 a_{3,5,6} - 0.079 a_{10,12,13} + 0.093 a_{13,12,14} + 0.048 a_{12,14,15} - \end{array}$	0.037a15,14,28 	933 - 0:00213,5 0:00012831 0:10041,34 0:11144,3,5 0:007493,56 1 0:07746,5,7 7.1 = 0.0334 0.0491 + 0.037a 0.035a	954 - 0.0010/2 00012831 0000 0556 0000000000000000000000000000	$q_{55} = -0.047r_{1,3} + 0.063r_{28,31} - 0.032a_{2,1,3} - 0.032a_{3,5,6} + 0.030a_{11,1,0,12} + 0.030a_{10,12,13} - 0.031a_{10,12} + 0.$	0.05181 <sub>31214</sub> 0 = 0.046f = 0.121f = 0.062a = 0.070a = 0.063a = 0.054a	95/ - 00001/2/ - 00001/2831 - 000042/2831 - 000042/281 - 000041/2731 - 000041/2731 - 000042/2812 960 = - 0.051fein + 0.061fein + 0.037agein - 0.033agens -	0.055a <sub>9,10,11</sub> + 0.032a <sub>11,10,12</sub> - 0.050a <sub>12,14,15</sub> + 0.040a <sub>15,14,28</sub>	$q_{61} = - \ 0.039r_{17,19} + 0.079a_{16,17,18} - 0.081a_{18,17,19} - $	$0.087a_{17,19,20} + 0.079a_{20,19,21} + 0.071a_{21,22,23} - 0.077a_{23,22,24} + 0.065a_{16,24,25} - 0.077a_{23,22,24} + 0.077a_{23,24} + 0.077a_{23,24} + 0.077a_{23,23} + 0.077a_{23,22,24} + 0.077a_{23,24} + 0.077a_{23,22,24} + 0.077a_{23,24} + 0.077a_{23,22,24} + 0.077a_{23,24} + 0.077a_{23,22,24} + 0.077a_{23,24} + 0.077a_{23,2$	0.065a <sub>22,24,25</sub>	$q_{63} = -0.035r_{7,27} + 0.061r_{8,16} - 0.045r_{28,31} - 0.030a_{7,27,31}$	$q_{64} = -0.034r_{7,27} - 0.034r_{28,31} + 0.037a_{2,1,3} - 0.032a_{2,1,27} - 0.031a_{1,3,4} - 0.021a_{2,1,3,7} - 0.031a_{1,3,4} - 0.031a_{1$	$0.05/a_{3,5,6} + 0.0/0a_{6,5,7} + 0.038a_{10,12,13} + 0.035a_{12,14,15} - 0.045a_{15,14,28} - 0.0057a_{15,14,28} - 0.0057a_{15,14,18} - 0.0057a_{15,14,18}$	0.030a7,27,31	$q_{66} = -0.032r_{9,10} + 0.036r_{9,28} - 0.043r_{14,28} + 0.057r_{28,31} + 0.036a_{1,3,4} - 0.039a_{3,5} + 0.046a_{5,6} - 0.044a_{5,5,7} + 0.032a_{1,1,4,5} - 0.049a_{1,5,1,2,8} + 0.032a_{7,7,31}$	$q_{69} = 0.047 r_{3,5} + 0.054 r_{3,31} + 0.037 a_{1,3,4} - 0.034 a_{4,3,5} + 0.038 a_{6,5,7} - 0.03$	$0.046a_{9,10,11} + 0.042a_{10,11,12} - 0.041a_{12,14,15} + 0.045a_{15,14,28} - 0.045a_{15,14,18} - 0.045$	$0.031a_{1,27,31} + 0.044a_{7,27,31}$	$q_{71} = 0.055r_{7,8} - 0.033r_{7,27} - 0.039r_{8,16} - 0.035r_{10,12} - 0.031a_{7,8,9} + 0.034a_{15,14,28}$	$q_{72} = -0.055r_{5,7} + 0.050r_{7,27} - 0.058r_{28,31} - 0.039a_{2,1,27} + 0.037a_{4,3,5} - 0.037a_{4,5} $	$0.034a_{3,5,6} + 0.063a_{1,27,31} - 0.046a_{7,27,31}$	$q_{74} = 0.054r_{1,3} - 0.037r_{3,5} - 0.035r_{14,28} + 0.036r_{28,31} + 0.042a_{2,1,27} - 0.042a_{2,1,17} - 0.042a_{2,1,17} - 0.042a_{2,17} - 0.0$	$0.052a_{1,3,4} + 0.053a_{4,3,5} - 0.032a_{12,14,15} + 0.033a_{15,14,28}$	$q_{79} = - \ 0.038 \ r_{8,9} - 0.035a_{16,17,18} + 0.038a_{18,17,19} - 0.035a_{17,19} \ _{20} + 0.031a_{20,19,21}$	$q_{80} = -\ 0.037r_{10,12} - 0.033a_{13,12,14} + 0.034a_{12,14,15} - 0.033a_{16,17,18} + 0.033a_{18,17,19} - 0.033a_{16,17,18} + 0.033a_{18,17,19} - 0.033a_{16,17,18} + 0.033a_{17,18} + 0.033a_{17,18} + 0.033a_{17,18} + 0.033a_{17,17,18} + 0.03$	$0.035a_{17,19,20} + 0.035a_{20,19,21} + 0.032a_{21,22,23} - 0.035a_{23,22,24} - 0.035a_{23,22} - 0.035a_{23,24} - 0.035a_{23$	0.038a <sub>16,24,25</sub> + 0.039a <sub>22,24,25</sub>	981 = 0.030r1,3 - 0.039r5,/ + 0.040r7,8 + 0.035r10,12 + 0.001r28,3 1 + 0.034a2,1,27 0.042a3 s s + 0.041as s 7 + 0.032a3 in 11 - 0.041a1 3731 + 0.045a37331
nt Raman cross-sectio	lated <sup>a</sup>	$d\sigma_{nRRS}/d\Omega^d$ [ $10^{-14}$ cm $^2$ sr <sup>-1</sup> ]	0.0152	0.0048	0.0105	0.0067	0.0100	0.0192	13000	0.0221		0.0059	0.0133	0.0024		0.0051			0.0193	0.0158			0.0801	0.1080			0.0802			0.0364		0.0199	0.0111			0/00/0
oerimental nonresona	Calcu	Wavenumber [cm <sup>-1</sup> ]	807	866	881	926	973	992	1031	1056		1080	1095	1160		1162			1199	1237			1260	1316			1352 + 1368			1398		1488	1492		L t t	CI CI
s and calculated and exp		$d\sigma_{n_{ m RRS}}/d\Omega^{ m f}$ (solid) [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	0.0189	0.0044	0 0095	0.0033	0.0059	0.0053	0.0181	0.013		0.0053	0.0073			0.0136			0.0479	I			0.0850	0.1007			0.1094			0.0418		0.0051	weak			0.0372
ents, mode description:	Experimental	$d\sigma_{n_{ m RRS}}/d\Omega^{ m b}$ (solution) [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]		I	I	I	I	I		I			I	I		I			Ι	l			0.0313	0.0310			0.0778			Ι		Ι	Ι			0.0395
Mode assignm		Wavenumber ( [cm <sup>-1</sup> ]	820	852	875	892	945	983	1011	1052	1	1077	1102			1179			1222				1279	1331			1385			1418		1508	1538			0061
Table 2.		Normal modes	36	42	44	46	49	51	53	с <b>Т</b>	5	55	57	60		61			63	64			66	69			71 + 72			74		79	80		ō	α

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Table 2.	(Conitnued)					
		Experimental		Calcul	ated <sup>a</sup>	Mode assignments <sup>e</sup>
Normal modes	Wavenumber [cm <sup>-1</sup> ]	d\sigma <sub>nRRS</sub> /dΩ <sup>b</sup> (solution) [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	$d\sigma_{nRRS}/d\Omega^{c}$ (solid) [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	Wavenumber [cm <sup>-1</sup> ]	$d\sigma_{nRRS}/d\Omega^{d}$ [10 <sup>-14</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	
32+83	1576	0.1125	0.1125	1530 + 1544	0.1083	$\begin{array}{l} q_{82}=-\ 0.031r_{7,8}+0.053r_{8,9}-0.034r_{14,28}-0.032a_{12,14,15}\\ q_{83}=-\ 0.030r_{8,9}-0.042r_{16,17}+0.043r_{16,24}+0.048r_{19,21}-0.046r_{21,22}-\\ 0.033a_{18,17,19}+0.036a_{17,19,20}-0.032a_{23,22,24}+0.035a_{22,24,25}\\ \end{array}$
84	1609	0.0221	0.0261	1590	0.0478	$\begin{array}{l} q_{84}=-\;\;0.037r_{16,17}-\;0.035r_{16,24}+\;0.067r_{17,19}-\;0.036r_{19,21}-\\ 0.039r_{21,22}+\;0.068r_{22,24}+\;0.034a_{17,16,24}+\;0.055a_{16,17,18}-\;0.038a_{18,17,19}-\\ 0.039a_{17,19,20}+\;0.056a_{20,19,21}+\;0.034a_{19,21,22}+\;0.057a_{21,22,23}-\\ 0.039a_{23,22,24}+\;0.055a_{16,24,25}-\;0.036a_{22,24,25}\end{array}$
<sup>a</sup> DFT/B3L <sup>b</sup> Raman c <sup>c</sup> Raman c <sup>4</sup> Raman c <sup>a</sup> Only con	YP 6–311G (2d,2 cross-sections we ross-sections we ross-sections we rtributions great	<ul> <li>p) with PCM model.</li> <li>are calculated using Eqn ( re calculated relative to t re calculated using Eqn ( re than 3% are displayed.</li> </ul>	(1). the 1576 cm <sup>-1</sup> band, assum (2) with the local field corre !	ing the cross-sections a ection factor applied.	re the same in the solu	ion and solid phases.

influence on the electronic properties of dipyrrin compounds and this is indeed the case.  $^{\rm [60]}$ 

## Surface-enhanced Raman spectra

There are a number of factors that affect the magnitude of the SERS enhancement. A complicating factor is the definition of the enhancement factor itself. Most studies of SERS enhancement factors define the *average* SERS enhancement factor as<sup>[61]</sup>

$$EF = \frac{I_{\rm SERS}/N_{\rm Surf}}{I_{\rm RS}N_{\rm Vol}}$$

where  $N_{Vol} = c_{RS}V$  is the average number of molecules in the scattering volume (*V*) for the non-SERS measurement and  $N_{Surf}$  is the average number of molecules *adsorbed* in the scattering volume for the SERS measurements. Le Ru *et al.* have presented the problems associated with this definition,<sup>[61]</sup> with the consequence being that there could be large variations in reported enhancement factors.

Silver nanoparticles prepared via the method reported by Lee and Meisel typically have a heterogeneous size distribution with diameters between 10–200 nm with various shapes such as rods and triangles.<sup>[62]</sup> To confirm the size and shape of our nanoparticles, we obtained TEM images of the silver nanoparticles used in the SERS measurements (Fig. S4).

Knowledge of the size and shape distribution of the nanoparticles enables an estimation of the concentration of the adsorbate required for monolayer coverage of the silver nanoparticles and therefore the SERS enhancement factors can be accurately calculated. TEM images such as shown in Fig. S4 were used to determine the number and types of nanoparticles (i.e. spherical nanoparticles vs nanorods), in a typical sample, along with an estimate of the variation in particle size (we thank one of the reviewers for this suggestion). In the samples that were analysed, approximately 70% were nanoparticles (diameter =  $48 \pm 9$  nm, most with well-defined crystal faces) and 30% were nanorods (diameter =  $41 \pm 7$  nm, length =  $84 \pm 28$  nm). The total available surface area can be expressed by assuming all nanoparticles are spherical with a diameter of  $52 \pm 10$  nm. These uncertainties, along with an estimate in the uncertainty of the Raman intensities, allow an estimate of the uncertainty in the enhancement factors reported below, which we estimate to be approximately 20%. The footprint of the dipyrrin molecule can be estimated using the DFT calculation. The ratio of the surface areas gives the number of dipyrrin molecules required per nanoparticle and finally the concentration of dipyrrin required for monolayer coverage.

For monolayer coverage of nanoparticles with a 52 nm effective diameter we estimate for  $N_{Surf}$  a value of  $3.02 \times 10^4$  dipyrrin molecules per silver nanoparticle. With the nanoparticle concentration estimated from the total silver concentration and average particle size, a dipyrrin concentration of 7.9  $\mu$ M is required for monolayer coverage.

Table 4 displays the Raman cross-sections for SERS and electronic and SERS enhancement factors for **1**. The observed SERS cross-sections are approximately 1–2 orders of magnitude larger than the resonant Raman cross-sections. Also, the corresponding electronic and SERS enhancement factors have similar relative values. This illustrates that for free dipyrrins systems, the majority of the enhancement has electronic origins at least for the conditions used in this study. From detailed studies of the SERS cross-sections and by considering the effects of preresonance enhancement, the maximum average SERS enhancement factors have been estimated to be in the range of  $10^{10}-10^{12}$ .<sup>[61]</sup> In this work no attempt was made to maximise the position of the



Figure 5. Selected normal modes of 1. Arrows represent the displacement of atoms.

plasmon resonance with respect to the excitation wavelength or to match the plasmon resonance with the molecular resonance frequency. The maximum values (approx.  $10^8$ ) reported here



**Figure 6.** Nonresonant Raman and resonant Raman spectra of **1** with normal modes assigned. Resonant Raman spectra were collected with (A) 444 nm excitation, (B) 458 nm excitation, and (C) 488 nm excitation. [S denotes solvent peaks ( $CH_2CI_2$ ), # denotes laser lines]. (D) Nonresonant Raman spectrum was recorded as a KBr pellet.

suggest that there is ample scope for improving the intensity of the SERS intensities of dipyrrin compounds.

The SERS spectra of **1** with mode assignments is given in Fig. 7. Modes were assigned based on the DFT calculation; however, there were discrepancies where there were interactions of some modes with the silver nanoparticle surface. For instance the modes 81 and 82 + 83 have significantly shifted wavenumbers but they can be assigned by a consistent downshift from the nonresonant spectrum.

As with the resonant Raman spectra of the free dipyrrin molecules, the SERS spectra show that most of the vibrational modes are enhanced. The pattern of enhancement is somewhat different and the strong enhancement of mode 54 is particularly evident along with modes 46, 51 and to a lesser extent, modes 63 and 64. We do not attempt a detailed analysis of the underlying enhancement mechanisms in this work (a wider range of excitation wavelengths would be required at least) but we can suggest possible explanations for the strong enhancement of mode 54. This arises from the interaction of 1 with silver nanoparticles. The different intensity patterns under the nonresonant, resonant and surface-enhanced conditions reflect the mechanisms responsible for generating the Raman scattering in each case. Under nonresonant conditions, the polarisability in the ground state controls the intensity of the observed modes, and therefore modes with large polarisabilities will have large intensities. Under resonant conditions, the origin of the electronic transition controls the mode intensities, and for strongly allowed electronic transitions, such as  $\pi - \pi^*$ , the scattering will be

Table 3.	Experimental Raman cro	oss-sections for nonre	sonant Raman a	nd resonant Raman da	ata, and resonan	t Raman enhancemen	t factors for <b>1</b>
		444 nm	ı	458 nm	ı	488 nm	1
Normal modes	Wavenumber [cm <sup>-1</sup> ]	$d\sigma_{\rm RRS}/d\Omega^{\rm a}$ [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	EF <sup>b</sup> [10 <sup>4</sup> ]	$d\sigma_{\rm RRS}/d\Omega^{\rm a}$ [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	EF <sup>b</sup> [10 <sup>4</sup> ]	$d\sigma_{\rm RRS}/d\Omega^{\rm a}$ [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	EF <sup>b</sup> [10 <sup>4</sup> ]
36	819	1 015	5.4	539	2.9	119	0.6
44	870	2 093	22.1	750	7.9	219	2.3
46	895	1 607	49.1	102	3.1	302	9.2
49	938	1 172	19.7	—	—	—	—
51	989	1 681	32.0	573	10.9	123	2.3
53	1 007	2 398	13.3	720	4.0	241	1.3
54	1 047	1 793	15.8	504	4.4	177	1.6
55	1 074	1 876	35.6	693	13.1	243	4.6
57	1 099	1 757	24.0	239	3.3	36	0.5
60	1 123	1 691	—	475	—	80	—
61	1 178	900	6.6	508	3.7	91	0.7
63	1 222	255	0.5	521	1.1	—	—
64	1 255	166	—	590	—	58	—
66	1 275	3 2 3 4	3.8	1 731	2.0	208	0.2
69	1 329	8 882	8.8	5 236	5.2	484	0.5
70	1 355	1 863	—	—	—	—	—
71 + 72	1 390	10 1 26	9.3	2 007	1.8	253	0.2
74	1 410	629	1.5	—		—	—
79	1 518	936	18.5	380	7.5	9	0.2
80	1 538	841	—	—		62	—
81	1 561	3 889	10.5	1 573	4.2	355	1.0
82 + 83	1 580	13 608	12.1	3 636	3.2	605	0.5
84	1612	544	2.1	42	0.2	10	0.04

<sup>a</sup>Raman cross-sections were calculated using Eqn (1) and the solvent band of dichloromethane at 701/740 as in <sup>[38]</sup>.

<sup>b</sup>*EF* = *Enhancement Factor* =  $(d\sigma_{\text{RRS}}/d\Omega)/(d\sigma_{\text{nRRS}}/d\Omega)$ .

<sup>c</sup>EFs are relative to the nonresonant (solid) Raman cross-sections.

dominated by Albrecht A-term scattering.<sup>[18]</sup> The selection rules for A-term dictate that only modes that are totally symmetric within the common group of the ground and excited states will be resonantly enhanced. Although the totally symmetric modes are only a subset of the modes that could appear in the nonresonant spectra, the large electronic enhancement factors mean that many modes that were below the level of noise in the nonresonant spectrum appear with significant intensity in the resonant Raman spectrum. A similar number of modes are observed between the resonant and surface-enhanced spectra. However, the pattern of enhancements is different and this is a result of additional enhancements from resonance with the plasmon modes of the silver nanoparticles. Under plasmon enhancement conditions, Herzberg–Teller coupling between the ground and other electronic excited-states of the system leads to enhancement of nontotally symmetric and totally symmetric modes and this explains the changes in the appearance of the resonant and surface-enhanced spectra. The same effect can be observed in comparing the differences in intensities obtained with different excitation wavelengths in the SERS measurements.

Table 4 shows that the SERS enhancement factors are greater with 488 nm excitation than with 458 nm excitation. This seems to be at odds with the peak of the silver plasmon resonance for the Lee and Meisel Ag nanoparticles around 420 nm. However, scattering from hot-spots dominates the total Raman scattering,<sup>[63]</sup> and plasmon coupling<sup>[64]</sup> between the small fraction of nanoparticles that form the hot-spots red-shifts the plasmon resonance. A possible explanation for the large SERS enhancements



Figure 7. Surfaced-enhanced Raman spectra of 1 on silver nanoparticles with normal modes highlighted. (A) 458 nm and (B) 488 nm.

at 488 nm is that the enhancement is dominated by the redshifted plasmon resonance. On the other hand at 488 nm excitation, electronic resonance with the  $\pi - \pi^*$  transition decreases, but this decrease is compensated for by an increase in the plasmon enhancement as the excitation moves to lower frequencies. Those modes that show noticeable changes in intensity between 458 and 488 nm excitations are modes 46, 50, 51, 79 and 81. Table 4. Normal modes and Raman cross-sections for experimental SERS data for 1

			458 nm			488 nm	
Normal modes	Wavenumber [cm <sup>-1</sup> ]	$d\sigma_{SERS}/d\Omega^{a}$ [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	Total EF <sup>b</sup> [10 <sup>4</sup> ]	Electronic <i>EF</i> <sup>d</sup> [10 <sup>4</sup> ]	$d\sigma_{SERS}/d\Omega^{a}$ [10 <sup>-28</sup> cm <sup>2</sup> sr <sup>-1</sup> ]	Total <i>EF</i> <sup>b</sup> [10 <sup>4</sup> ]	Electronic <i>EF</i> <sup>d</sup> [10 <sup>4</sup> ]
18	402	6 499					
19	410	10618					
21	454	1 055					
22	492	2851					
23 + 24	587	398			11 985		
25	603	1 503					
27	655	5916			8126		
29	697	4 946			9734		
31 + 32	726	1 4 1 5			2411		
35	772	4 2 4 4			6 0 9 8		
36	822	4863	25.8	2.9	1 688	9.0	0.6
44	872	7 504	79.2	7.9	18 483	195.2	2.3
46	903	11 464	350.0	3.1	18 270	557.8	9.2
51	990	13 528	257.5	10.9	21 903	416.9	2.3
53	1 021	9 326	51.6	4.0	11 255	62.3	1.3
54	1 054	30 036	264.8	4.4	97 646	861.0	1.6
61	1 1 7 3	4 187	30.7	3.7	9864	72.4	0.7
63	1 207	5 738	12.0	1.1	9672	20.2	
64	1 238	15 177			22 375		
69	1 338	4 500	Undefined <sup>e</sup>	5.2	17 404	17.3	0.5
71	1 389	7 236	6.6	1.8	9607	8.8	0.2
79	1 485	1 758	34.7	7.5	2 0 9 3	41.3	0.2
81	1 525	7 822	21.0	4.2	14689	39.5	1.0
82 + 83	1 555	19782	17.6	3.2	67 653	60.1	0.5
84	1 609	5 707	21.8	0.2	12914	49.4	0.04

<sup>a</sup>Raman cross-sections were calculated using Eqn (2) and Na<sub>2</sub>SO<sub>4</sub> as an external reference.<sup>[41]</sup>

<sup>b</sup>Total Enhancement Factor =  $(d\sigma_{SERS}/d\Omega)/(d\sigma_{nRRS}/d\Omega)$ .

<sup>c</sup>EFs are relative to the nonresonant (solid) Raman cross-sections.

<sup>d</sup>Electronic Enhancement Factor =  $(d\sigma_{RRS}/d\Omega)/(d\sigma_{nRRS}/d\Omega)$ .

<sup>e</sup>Obscured by laser line.

# Conclusion

With strong resonant enhancement, negligible fluorescence, facile synthetic chemistry and an established track record in biological applications, dipyrrins display all the desired properties for not only fundamental studies of SERS but a range of bioanalytical applications.

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### **Supporting information**

Supporting information may be found in the online version of this article.

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