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Vibrational properties of new corrole-fullerene dyad and its components

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ABSTRACT

We present first systematic spectral studies of a new corrole-fullerene dyad and its components: modified corrole and suitable spacer. The infrared absorption and Raman scattering spectra were measured in polycrystalline samples, at room temperature. Quantum chemical calculation results were compared with the experimental IR and Raman spectra. An attribution of the strongest IR and Raman bands was proposed. It was found that the strongest excitations in the dyad are mainly related to the excitations of the modified corrole part with some influence from the spacer and fullerene parts. © 2012 Published by Elsevier Ltd.

1. Introduction

Design and characterization of electronic components with molecular dimensions is an area of extensively active studies. The reason of these investigations is to enquire about new artificial molecular systems mimicking the primary phenomena of natural photosynthesis. Photosynthesis has been widely investigated not only for understanding all aspects of this fascinating process [1] but also by reason of its potential applications – for construction of organic solar cells [2–6]. Organic cells are the most promising devices taking advantages of the artificial photosynthesis effect.

Dyads containing an organic chromophore (working as an electron donor) bonded to an electron acceptor (e.g. fullerene) are active materials in the simplest solar cells. The excellent electron-accepting capability of fullerenes renders them attractive building blocks for organic solar cells [7]. On the other hand, porphyrinoids [8] are perfect and commonly used chromophores in these solar cells. Meso-substituted corroles are recently among the most widely investigated compounds, in this regard [9–12].

Corroles are one C atom fewer analogues of porphyrins possessing the skeleton of corrin with three *meso*-carbons between the

* Corresponding author. E-mail address: barszcz@ifmpan.poznan.pl (B. Barszcz). intense absorption of red light [13,14]. Free-base corroles reveal the Soret-type absorption in the 400–440 nm region and Q band transitions between 500 and 700 nm. The absorption spectra of corroles exhibit two important differences versus porphyrins. Firstly, there is more pronounced change in the optical absorption of the corroles upon variation of the substitution on the phenyl group than in the corresponding porphyrins and secondly, corroles exhibit very significant solvent-dependent absorptions in contrast to the small shifts typically detected in porphyrins [15]. It is necessary to notice, that the effect of substitution on the optical properties of corroles is significantly larger than in porphyrins. Finally, corroles can be highly emissive, with high quantum yields of fluorescence [9,13–15]. The corroles are, in general, less stable

four pyrrole rings [9]. When compared with porphyrins, these tribasic aromatic macrocycles exhibit lower oxidation potentials,

higher fluorescence quantum yields, larger Stokes shifts, and more

the corresponding component corroles [10]. The comprehensive spectral investigations of corroles and their dyads with the fullerene are very important because the knowledge of vibrational and electronic properties of these materials facilitate appropriate selection of molecular systems for designing solar cells. Besides, there are only a few papers describing selected aspects of the IR or Raman spectra of some corroles [16–19]. Vibrational spectral studies of a few corroles were recently reviewed in [20].

than porphyrins but the stability of their dyads is better than that of





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In this paper we present unique investigations of the vibrational properties of the new fullerene-corrole dyad ($\mathbf{6}$) and its components ($\mathbf{3}, \mathbf{4}$). Spectral investigations of IR absorption and Raman scattering were compared with quantum chemical calculations. According to our knowledge there are first complex spectral investigations of the dyad and its components.

2. Experimental section

2.1. General experimental

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH₂Cl₂, hexanes, cyclohexane) were distilled prior to use. All reported ¹H NMR and ¹³C NMR spectra were recorded on Bruker AM 500 MHz or Varian 400 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. UV–Vis spectra were recorded in CH₃CN. Chromatography was performed on silica (Kieselgel 60, 200–400 mesh) or size-exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX-1 with toluene as eluent. Mass spectra were obtained *via* electrospray MS (ESI-MS). Pentafluorophenyldipyrrane was synthesized according to the literature procedure [21].

2.2. 2,3,5,6-Tetrafluoro-4-(4-formylphenyloxy)benzaldehyde (3)

Pentafluorobenzaldehvde (1. 1.59 mL 10 mmol) was slowly added to a mixture of 4-hydroxybenzaldehyde (2, 1.22 g, 10 mmol). cesium fluoride (3.04 g. 20 mmol) and anhydrous DMF (20 mL) under an argon atmosphere. The reaction mixture was stirred for 1 h at RT and then diluted with water and ethyl acetate. Subsequently the aqueous layer was washed three times with ethyl acetate. Combined organic layers were washed with water and brine, dried with anhydrous Na₂SO₄ and concentrated. The product was purified by the column chromatography using methylene chloride as an eluent. After the solvent evaporation, 1.76 g of white solid was obtained (59%). Mp: 85–86 °C. ¹H NMR (500 MHz, CDCl₃): δ 10.32 (t, ¹H – ¹⁹F coupling, ⁴J_{1H,19F} = 2.1 Hz, 1H), 9.98 (s, 1H), 7.93, 7.14 (AA'XX', 2 × 2H), ¹³C NMR (125 MHz, CDCl₃): δ 190.3, 181.7, 160.5, 148.6, 146.5, 142.2, 140.2, 137.7, 133.0, 132.1, 116.2, 112.1. HRMS (EI 70 eV) calcd for C₁₄H₆F₄O₃ (M⁺): 298.0253, found: 298.0256. Elemental analysis calcd (%) for C₁₄H₆F₄O₃: C 56.39, H 2.03; found: C 56.07, H 2.30.

2.3. Corroles 4 and 5

A mixture of water (200 mL) and c.HCl (10 mL) was added to a stirred solution of 3 (0.596 g, 2.0 mmol) and pentafluorophenyldipyrrane (1.250 g, 4.0 mmol) in methanol (200 mL). After 30 min of stirring at RT, the reaction mixture was diluted with chloroform. The aqueous layer was extracted with chloroform, combined organic layers were washed twice with water, dried over sodium sulphate, concentrated to a volume of 40 mL and placed into 40 mL syringe. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.180 g, 5.2 mmol) was dissolved in a minimum volume of toluene, diluted to 40 mL with methylene chloride and placed into second syringe. The contents of each syringes were simultaneously added dropwise to vigorously stirred methylene chloride (50 mL) for 10 min at room temperature (the same rate of addition from both syringes is crucial). After complete addition the reaction was continued for 15 min. Solvents were then evaporated and products were separated by the column chromatography (hexanes:methylene chloride 1:1). Two regioisomers were obtained: Corrole **4**: 0.493 mg (27%). Mp: 237–239 °C. ¹H NMR (500 MHz, CDCl₃): δ 10.36 (s, 1H), 9.12 (d, J = 4.0 Hz, 2H), 8.73 (d, J = 4.6 Hz, 2H), 8.68 (d, J = 4.6 Hz, 2H), 8.58 (d, J = 4.0 Hz, 2H), 8.17 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ –137.9 (d, J = 17.6 Hz, 2F), -144.6 (dt, J = 13.1, 4.5 Hz, 1F), -152.5 (dt, J = 13.1, 4.5 Hz, 1F), -152.7 (t, J = 19.1 Hz, 1F), -161.7 (t, J = 18.5, 2F). HRMS (ESI) calcd for C₄₄H₁₇F₁₄N₄O₂ (M + H⁺): 899.1122, found: 899.1150. **Corrole 5**: 0.202 mg (11%). Mp: >400 °C. ¹H NMR (500 MHz, CDCl₃): δ 10.04 (s, 1H), 9.08 (s, 2H), 8.82 (d, J = 4.2 Hz, 2H), 8.69 (d, J = 4.2 Hz, 2H), 8.54 (s, 2H), 8.06 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H). HRMS (FD-TOF) calcd for C₄₄H₁₆F₁₄N₄O₂ (M⁺): 898.1050, found: 898.1082.



Scheme 1. The synthesis of formyl-corroles 4 and 5.



Scheme 2. The synthesis of corrole-fullerene dyad 6.

2.4. Corrole-fullerene dyad (6)

Aldehyde **4** (180 mg, 0.2 mmol), C_{60} (144 mg, 0.2 mmol) and sarcosine (89 mg, 1 mmol) were placed in 100 mL Schlenk flask and argonated (*purge-and-refill* technique). Dry, air-free toluene (25 mL) was added and obtained mixture was stirred for 20 h at 120 °C. Then, toluene was evaporated and the residue was passed through a silica gel pre-column (heptane:toluene, 1:1). Finally, the product was separated by the preparative size exclusion column

chromatography (SEC, toluene as an eluent). After the solvent evaporation 65 mg of black solid was obtained which was then recrystallized from toluene/heptane to give 49 mg (15%) of **6** as a black powder. Mp: >400 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.83 (s, 2H), 8.53 (d, *J* = 4.6 Hz, 2H), 8.44 (d, *J* = 4.6 Hz, 2H), 8.36 (s, 2H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 5.45 (s, 1H), 4.48 (d, *J* = 9.6 Hz, 1H), 3.73 (dd, *J* = 9.6, 2.6 Hz, 1H), 2.64 (s, 3H). LRMS (FD-TOF) calcd for C₁₀₆H₂₁F₁₄N₅O (M⁺): 1645, found: 1645 as high purity amorphous powders obtained by chromatography and characterized by ¹H NMR spectroscopy.

The vibrational IR absorption spectra of the corrole-based-fullerene dyad (**6**) and its main components (**3**, **4**) were investigated at room temperature in polycrystalline powder. The investigations were performed with an FT-IR Bruker Equinox 55 spectrophotometer within the range 400–7000 cm⁻¹. Raman scattering spectra of the investigated compounds were recorded with Bruker IFS 66 FRA 106 spectrophotometer at room temperature, with laser excitation $\lambda_{exc} = 1064$ nm. Additionally, the Raman spectra were recorded using LabRAM HR 800 spectrophotometer (HORIBA Jobin Yvon) with excitation $\lambda_{exc} = 488$ and 514 nm from the Stabilite 2017 Ar laser. The power of the laser beam at the sample in all cases was less than 1 mW with a power density of about 3×10^8 mW cm⁻². Such a low power density was necessary to avoid decomposition of the sample.

In order to realize of an optimal structure of the compounds and to interpret the experimental results of IR absorption and Raman scattering investigations quantum chemical calculations were performed. The molecular geometries were optimized using the Density Functional Theory (DFT) method with B3LYP hybrid functional and 6-31G and 6-31G(d) basis sets. The calculations of normal mode frequencies and intensities were also performed. All calculations were made using Gaussian 03 package [22]. The GaussView program was used to propose an initial geometry of investigated molecules and for visual inspection of the normal modes.

3. Results and discussion

We designed the fullerene-corrole dyad 6 based on the following principles: (a) two C₆F₅ units should be present at positions 5 and 15 of corrole core to ensure high stability; (b) the semirigid spacer should link both chromophores. Diaryl ether linker appeared to fullfill these conditions. The key intermediate (dialdehyde 3) was prepared by the nucleophilic aromatic substitution p-hydroxbetween pentafluorobenzaldehyde (1) and ybenzaldehyde (2) in the presence of cesium fluoride as a base (Scheme 1). In agreement with previously published methodology [23] only the product of fluorine atom substitution at position 4 was obtained. In the next step, dialdehyde 3 was converted into trans-A₂B-corrole using the modified H₂O/MeOH/HCl [24] method,



Scheme 3. Optimized geometry of the investigated newly synthesized fullerene–corrole dyad (6) and its components (3, 4). Theory level B3LYP/6-31G. Note: grey – carbon, red – oxygen, blue – nitrogen, white – hydrogen, cyan – fluorine.

in which dipyrrane reacts with an aldehyde and subsequently crude tetrapyrrane is oxidized with DDQ. Due to the fact, that aldehyde **3** has two different formyl groups, the reaction with penta-fluorophenyldipyrrane leads to the formation of two regioisomeric corroles **4** and **5** (Scheme 1). Quite surprisingly, the yield of corrole **4** (28%) was significantly higher than the yield of corrole **5** (11%). Apparently steric hindrance imparted by fluorine atoms had more pronounced effect on the reactivity of the carbonyl group than electron density. Structures of these products were assigned after the comparision of their formyl protons shifts on ¹H NMR spectra with shifts of starting aldehyde **3**, whose formyl groups signals can be easily distinguished due to the ¹H–¹⁹F coupling.

Corrole–fullerene dyad **6** was synthesized in 15% yield, by the Prato reaction of corrole **4** with formaldehyde and sarcosine (Scheme 2). The product was purified by size exclusion chromatography (SEC). In analogy to another corrole–fullerene dyad [9] compound **6** is unstable when both light and oxygen are present. The optimal configurations of the investigated molecules **3**, **4**, and **6** are shown in Scheme 3.

The quantum chemical calculations of the normal modes of vibrations permit us to assign the bands observed in the experimental spectra to specific vibrations of various functional groups of the molecule. The experimental results were compared with calculations obtained using two different basis sets (6-31G and 6-31G(d)). The comparison shows that the results of calculations with the base 6-31G are more consistent with the experimental spectra (Fig. 1). Therefore, the interpretation of the spectra and assignment of vibrational bands were based on the results obtained with 6-31G base. In general, conformity between the calculated and experimental spectra is quite good. The wavenumber shifts between them are typical and arise from approximations used in the computational procedure. Mainly the anharmonicity of vibrations and environment of the molecules which are neglected in our calculations cause those shifts.

In Fig. 1 the experimental and calculated infrared spectra of the samples **3**, **4**, **6** in the spectral ranges 400–1900 and 3200–3500 cm⁻¹ are presented. The most significant is the region 600–1800 cm⁻¹ where intense and characteristic bands related to intramolecular vibrations of the molecules are observed, including the deformation of benzene and pentafluorobenzene C_6F_5 rings as well as stretching of various C–C bonds. Some information follows from an analysis of the bands located at about 3000 cm⁻¹, where the stretching vibrations of C–H bonds and the stretching of N–H bonds at corrole ring are observed.

In the calculated infrared spectrum of the dialdehyde 3 (Fig. 1a) a strong band at 1238, related to the in plane bending of C–C–H bonds in benzene ring is observed. Its counterpart in the experimental spectrum is located at 1230 cm⁻¹. The bands related to the out of plane bending of C-C-H bonds in the benzene ring are expected at 852 and 875 cm^{-1} but in the experimental spectrum they are seen at 825 and 854 cm^{-1} . The most intense band in the experimental spectrum is the doublet at $1597/1646 \text{ cm}^{-1}$; this is mainly due to the in-plane stretching vibrations of the C=C bonds in the benzene ring with some influences of the C=C stretching in C₆F₄ ring and C–C–H bending vibrations (calculated wavenumbers 1629 and 1657 cm^{-1}). The medium band at 955 cm^{-1} in the calculated spectrum related to the stretching of C–C bonds in C₆F₅ ring is stronger in the experimental spectrum and observed at 948 cm⁻¹. The calculated bands in the spectra of dialdehyde **3** at about 1007 and 1420 cm⁻¹ correspond to the experimental bands at 1006 and 1393 cm^{-1} and they are related to the stretching of C-F and C–C bonds in the C_6F_4 ring. The weak band related to the bending mode of C=O-H bond is observed at 1457 cm⁻¹ (1425 cm⁻¹ in experiment). The characteristic strong bands at 1705 and 1713 cm^{-1} are related to the C=O stretching vibrations in the

а Absorbance / Intensity calculations (B3LYP/6-31G 600 1400 1600 1800 3000 3500 800 1000 1200 Wavenumber (cm⁻¹) b Absorbance / Intensity 3000 3500 600 800 1000 1200 1400 1600 1800 Wavenumber (cm⁻¹) С Absorbance / Intensity s (B3LYP/6-31 600 800 1000 1200 1400 1600 1800 3000 3500 400 Wavenumber (cm⁻¹)

Fig. 1. IR absorption spectra of the fullerene–corrole dyad components (**3** (a), and **4** (b)) and the dyad (**6** (c)) at room temperature in polycrystalline powder. The appropriate calculated IR absorption spectra (B3LYP/6-31G) are also added in each panel.

aldehyde –CHO group. In the experimental spectrum they form a doublet with the maxima at 1695 and 1705 cm⁻¹. Besides, we observed a medium strength band at 1121 cm⁻¹ and strong one at 1488 cm⁻¹ related to the stretching of the C–O bonds between the benzene and C_6F_5 rings, which are located in the calculated spectrum at 1149 and 1508 cm⁻¹. The weak bands at about 2879 and 3370 cm⁻¹ are related to the stretching of the C–H bond in aldehyde –CHO group.

IR absorption spectra of the 4 and 6 are presented in Fig. 1b and c, respectively. The specific differences in the positions of calculated and experimental bands are gathered in Table 1. Bonding of the modified corrole **4** with the fullerene C_{60} by the diarylether spacer causes some changes in positions and intensities of the bands of the spacer. For example the stretching mode of C=O observed for 3 at 1705 cm^{-1} is shifted to 1707 cm $^{-1}$ for **4**; this mode is not observed in the dyad 6, because the aldehyde –CHO group has been replaced by a modified fullerene connected with C_6F_4 tetrafluorobenzene ring by pyrrol ring. The bands associated with the stretching of the C–H bonds in the CH₂ groups are observed at 2779 and 2848 cm⁻¹, but the stretching of the C–H bonds in the methyl group – at 2793 and 2871 cm⁻¹. A strong band related to the scissoring mode of – CH₂ and -CH₃ groups is located at 1517 cm⁻¹. Weak bands corresponding to the stretching of C–N bond in the pyrrol ring are observed at about 1550 cm⁻¹. In the calculated spectrum the adequate bands are registered at 2988, 3078, 3031, 3123, 1532, and 1583 cm⁻¹, respectively. In the spectrum of **6** we observe the bands related to the bending mode of C–C–N bond in pyrrole ring at 1247 cm^{-1} (according to calculations at 1299 cm^{-1}). The calculated band related to in-plane bending of C–C–H bonds in the benzene ring is observed at 1240 cm⁻¹ and 1243 cm⁻¹ (experimental at 1202 cm^{-1} and 1208 cm^{-1}), for **4** and **6**. The bands due to out of plane bending of the C–C–H in the benzene ring are observed at 856 and 847 cm^{-1} in experimental spectra of **4** and **6**, respectively. For **4** and **6** the in-plane stretching vibrations of the C=C bonds in the benzene ring with some influences of the C=C stretching in C_6F_4 ring and C–C–H bending vibrations are located at 1627 cm⁻¹ (1600 \mbox{cm}^{-1} in the experiment), 1655 \mbox{cm}^{-1} (1645 \mbox{cm}^{-1} in the experiment), 1634 cm^{-1} (experimental 1602 cm^{-1}) and 1658 cm^{-1} (experimental 1648 cm^{-1}), respectively. The band related to the stretching of C–C bonds in C_6F_4 ring for **4** is shifted by 5 cm⁻¹ in relation to 3 and is located in the experimental spectrum at 953 cm^{-1} (in the calculated spectrum we see this band at 955 cm⁻¹). The bands related to the stretching mode of C–O bond are located at 1488 and 1492 cm^{-1} for **4** and **6**, respectively. The first band attributed to the stretching of C–F bonds in the C_6F_4 ring observed for **3** at 1006 cm⁻¹ is shifted to 1016 cm⁻¹ for **4** and 1019 cm^{-1} for **6**. The second band of this vibration mode located at 1393 cm⁻¹ for **3**, is observed only for **4** at 1398 cm⁻¹. The absence of this band in the IR spectrum of **6** is attributable to stiffening of the C-F bonds in the pyrrole ring by linking to the fullerene. For 4 and 6 we observe strong band located at about 3260–3300 cm⁻¹ and attributed to stretching of C–H bonds in pyrrole ring in corrole; this band is stronger than that observed in calculated spectra. In the experiment for both **4** and **6** dvads we observe the strong band at 3363 cm⁻¹ related to the stretching of N–H bond in corrole ring. For these molecules the bands related to the bending of C–N–H bonds in the corrole ring are located at about 1600 cm^{-1} . The stretching of C–F bonds in the pentafluorobenzene C_6F_5 rings is the origin of band located in calculated spectra of **4** and **6** at 1536 cm⁻¹. For the dvad 6 we also observed the bands related to the deformations of the fullerene C₆₀. According to our calculations these bands should be observed at 550–570, 945, 1214, 1464 cm^{-1} and in the range 1619–1627 cm⁻¹. Of course, these vibrations are complex and involve not only the fullerene cage but also other parts of molecule

Table 1

Selected experimental (**bold**) and calculated normal vibrational modes of the investigated molecules. Notation: s-stretching, b-bending, sc-scissoring, ip-in plane, op-out of plane.

3 (cm ⁻¹)		4 (cm ⁻¹)		6 (cm ⁻¹)		Band assignment
IR exp /calc	Raman exp /calc	IR exp /calc	Raman exp /calc	IR exp /calc	Raman exp /calc	
854 /875		856 /844		847 /843		C–C–H b op benzene ring
	861 /865					C–C s in benzene ring
		928 /953		927 /953		def. corolle rings
948 /955		953 /955				$C-C \ s \ in \ C_6F_4 \ ring + C-F \ s$
1006/1007		1016/1007		1019/973		$C-F$ s in C_6F_4 ring
1121 /1149		1119 /1149				C-0 s
1209/1211	1209/1211	1173 /1213		1167/1213		C-O s + C-C-H bip benzene ring
1230/1238		1202 /1240		1208 /1243		C–C–H b ip benzene ring
				1247/1299		C-C-N b in pyrrole ring
	1312 /1334					$C-F$ b in C_6F_4
1393/1420	1393 /1420	1398/1420	1403/1420		1423 /1420	$C-Fs + C-Cs in C_6F_4 ring$
1425/1457		1433/1455				C=O-H b
1488/1508	1488/1508	1488 /1507		1492/1508	1502/1498	C-0 s
				1517 /1532	-/1532	$CH_2 sc + CH_3 sc$
		1521/1536	1524/1536	1519 /1536	1527 /1536	$C-F$ s in C_6F_5 ring
			,	1550 /1583	1560 /1583	C–N s in pyrrole ring
1597/1629	1597/1629	1600/1627	1597/1627	1602 /1634		C=C s ip in benzene ring
1646 /1657	1646 /1657	1645 /1655	1646 /1655	1648 /1658	1648/1658	C = C s ip in benzene ring
1695 /1707	1695 /1707					C=0 s
1705 /1713	1705 /1713	1707/1711	1708/1711			C=0 s
	,	,	,	2779 /2988		$C-H$ s in $-CH_2$ group
				2793 /3031		$C-H$ s in $-CH_3$ group
				2848 /3078		$C-H$ s in $-CH_2$ group
				2871 /3123		$C-H$ s in $-CH_3$ group
2879/2970	2879 /2970					C-H s in -COH group
2923 /3052	2923 /3052					C-H s in $-COH$ group
,	1			2951 /3151		N–H s in corrole ring
		3363 /3651		3363 /3648		N–H s in corrole ring

like $-CH_3$ group. Additional details of assignment can be found in Table 1.

Concluding the analysis of the infrared vibrational spectra of the investigated molecules one can see relatively good conformity between the experimental and calculated spectra. On the other hand the spectral changes caused by bonding the corrole with the C_{60} molecule are distinct and characteristic – the bonds involved in formation of the fullerene-corrole dyad are usually weakened – it results in hypsochromic shifts of the adequate bands. Some of them, e.g. C–F vibration of the C_{6F4} ring are shifted by 10–15 cm⁻¹.

The calculated and experimental Raman spectra of 3, 4 and 6 are presented in the Fig. 2. It is necessary to notice that Raman spectra of the samples **4** and **6** were very hard to obtain. Our attempts to measure the spectra with excitation lines 633 nm (from the He-Ne laser), 488 nm, and 514 nm (from the argon ion laser) were unsuccessful. The only excitation that allow us to get any result was the excitation line from the Nd:YAG laser (1064 nm). In general, the agreement between the experimental and calculated spectra was better in the case of IR spectra than Raman scattering. However, we were able to identify and assign the most important bands observed in the spectra to appropriate normal modes of vibration. In the Fig. 2a the Raman scattering spectra of 3 obtained with two excitations (488 and 514 nm) are presented together with the calculated spectrum. In the calculated Raman spectrum of 3 the dominant vibrations are the in-plane stretching of C=C bonds in benzene ring at 1629 and 1657 cm⁻¹, that corresponds very well with IR bands and that are observed in the experimental spectrum at 1597 and 1646 cm^{-1} . The other intensive bands observed in the experimental spectra at 1695 and 1705 cm⁻¹ are related to the stretching of C=O bonds and they are located in the calculated spectrum at 1707 and 1713 cm⁻¹, respectively. The band located in calculated spectrum at 1420 cm^{-1} is due to the stretching of C–F and C–C bonds in C_6F_4 ring. In experimental spectra of **3**, **4** and **6** this band is observed at 1393, 1403 and 1423 cm⁻¹, respectively. In the experimental Raman scattering spectrum of **3** we observe also distinct bands at 2879 and 2923 cm⁻¹ related to the stretching vibration of C–H bond in –COH group (calculated wavenumbers 2970 and 3052 cm^{-1} , respectively). The region 2500–3600 cm^{-1} is not shown to preserve the clarity of the picture. The bands observed at about 1200 cm⁻¹ are related to the stretching of C–C bonds in benzene ring. The bands observed in the experimental spectra at Raman Shifts lower than 800 cm⁻¹ are quite distinct but unfortunately their intensities in the calculated spectra are very low what makes the interpretation uncertain.

The vibrations characteristic for 3 can also be found in the spectra of 4 and 6. However their positions are slightly changed and in many cases the vibrations involve also other parts of the molecule. In experimental Raman scattering spectrum of **4** we observe a quite strong band at 1646 $\rm cm^{-1}$ and very weak band at 1597 $\rm cm^{-1}$ related to the stretching vibration of C=C bonds in the benzene ring. These bands in **6** are observed at 1648 cm⁻¹ and 1601 cm⁻¹. In the experimental spectra of **4** and **6** we observe quite strong bands at 1524 and 1527 cm^{-1} related to the stretching of C–F bonds in C₆F₅ ring. Besides, in calculated Raman scattering spectra of these two samples at 1583 cm⁻¹ we observe very strong band related to the vibration involving stretching of C–C bonds and bending of C– C–H bonds in corrole ring, but it is not observed or is very weak in experimental spectra. Quite weak bands observed between 1150 and 1400 cm⁻¹ are related to the stretching of C–C and bending of C–C=C bonds in corrole ring. Also, in this region the bands related to the rocking, wagging, and twisting vibrations of CH₂ and CH₃ groups and stretching vibration of C-F in C₆F₄ ring are located. The band related to the bending vibration of the C-H bonds in CH₃ group in **6** is clearly visible in calculated spectrum at 1106 cm^{-1} and it corresponds quite well to the band at 1074 cm⁻¹ observed in the



Fig. 2. Raman scattering spectra of the fullerene–corrole dyad components (**3** (a), and **4** (b)) and the dyad (**6** (c)) recorded at room temperature with excitations $\lambda_{exc} = 488$, 514, and 1064 nm. The calculated Raman scattering spectra (B3LYP/6-31G) of investigated molecules are added for comparison.

experimental spectrum. Very strong band related to the various vibrations of the C–C bonds in fullerene cage in experimental spectrum is located at 1462 cm⁻¹ and it is observed in calculated spectrum at 1475 cm⁻¹. This band is characteristic for the many

functionalized fullerenes and it was observed by us in many different samples at almost the same position [25-28]. Weaker but also clearly visible band related to the fullerene molecule vibration is observed at 1172 cm⁻¹ (in calculated spectra at 1170 cm⁻¹).

Summarizing the Raman scattering investigations we can say that in this case, Raman spectra are rather the addition to the IR absorption measurements. Of course the spectra are valuable because they give us some extra information about the vibrational behaviour of the sample but the IR is the main source of interpretation in this case. Especially the assignment of the bands with very low Raman activity is uncertain. Nevertheless, the infrared absorption together with Raman scattering spectra allow us to assign the most important bands of new corrole-fullerene system.

4. Conclusions

New corrole–fullerene dvad (6) and its components (3, 4) were synthesized and investigated using the infrared absorption and Raman scattering spectroscopies. We unexpectedly found that even moderate steric factors can play bigger role in aldehydes' reactivity than electronic factors. The experimental methods were supported by the quantum chemical calculations of the equilibrium geometry and normal mode vibrations of the investigated molecules. The experimental results are in quite good agreement with the DFT predictions. It was shown, that change in molecular structure of the dye leads to specific changes in the spectra. The most of the normal mode vibrations of the corrole and spacer can be also found in the spectra of the dyad. However, their positions and intensities are changed because of the linking with the fullerene molecule. Some vibrations of terminal groups of spacer do not appear in the dyad spectra because these groups are responsible for covalent link with the rest of the dyad. The presence of specific functional groups in the corrole molecule makes the spectral identification possible.

Spectrally observed effects authorized us to state that vibrational spectroscopy methods (especially infrared absorption) can be successfully used for characterization of such complex molecular systems as fullerene–corrole dyads.

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