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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.

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

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In this paper we present unique investigations of the vibrational properties of the new fullerene-corrole dyad (**6**) and its components (**3**, **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

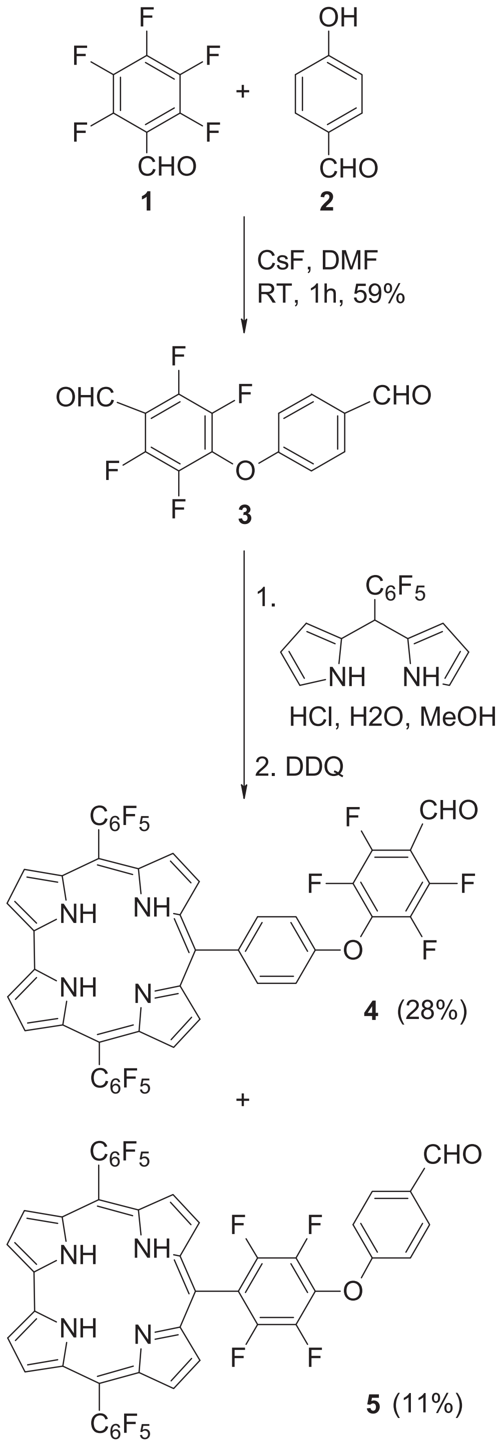
All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes, cyclohexane) were distilled prior to use. All reported ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AM 500 MHz or Varian 400 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; J values are given in Hz. UV–Vis spectra were recorded in CH_3CN. 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)***

Pentafluorobenzaldehyde (**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 Na_2SO_4 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, $CDCl_3$): δ 10.32 (t, $^1H-{}^{19}F$ coupling, $^4J_{1H,19F} = 2.1$ Hz, 1H), 9.98 (s, 1H), 7.93, 7.14 (AA′XX′, 2 × 2H), ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{14}H_6F_4O_3$ (M^+): 298.0253, found: 298.0256. Elemental analysis calcd (%) for $C_{14}H_6F_4O_3$: 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, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): 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 $C_{44}H_{17}F_{14}N_4O_2$ ($M + H^+$): 899.1122, found: 899.1150. **Corrole 5**: 0.202 mg (11%). Mp: >400 °C. ^1H NMR (500 MHz, $CDCl_3$): 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 $C_{44}H_{16}F_{14}N_4O_2$ (M^+): 898.1050, found: 898.1082.



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