



# High first hyperpolarizability and perfectly aligned crystal packing for an organometallic compound $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)((\text{R})\text{-PROPHOS})(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2$

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## Abstract

The molecular first hyperpolarizability,  $\beta$ , and the X-ray crystal structure of the complex  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)((\text{R})\text{-PROPHOS})(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{PF}_6]$  ((R)-PROPHOS = (R)-(+)-bis-(1,2-diphenylphosphino)propane) were determined. A near-resonant enhanced  $\beta$  value as high as  $545 \times 10^{-30}$  esu was obtained from hyper-Rayleigh scattering measurements. In addition, the compound crystallizes in the space group P1 with a perfect alignment of the dipolar molecules (only a single chromophore per unit cell), thus maximizing the macroscopic nonlinearity for electro-optic or parametric frequency conversion applications. The molecular packing in the crystal is analyzed in order to understand the factors leading to the perfect alignment.

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## 1. Introduction

In the last decades, organic and more recently organometallic molecules have been widely studied

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for their interesting second-order nonlinear optical (NLO) properties [1,2]. Typically, a conjugated chain, providing a high (nonlinear) polarizability, is combined with electron donor and acceptor substituents (so called D- $\pi$ -A or push-pull systems) that provide the necessary asymmetry to obtain a nonzero second-order response (molecular hyperpolarizability  $\beta$ ). Even more possibilities are offered by organometallic molecules as their strong charge-transfer transitions allow for even larger polariz-

abilities, and can be tuned by varying the metal ion or ligands to take advantage of near-resonant enhancement. However, in order to achieve a high macroscopic nonlinearity (second-order susceptibility  $\chi^{(2)}$ ), which is proportional to the tensorial sum of the hyperpolarizabilities of the microscopic building blocks, the NLO chromophores also need to be oriented favorably in a macroscopically noncentrosymmetric structure. In fact, the first organometallic materials (ferrocene derivatives) for which significant macroscopic second-order NLO responses were found [3], owe their NLO response largely to their noncentrosymmetric crystal structure, even though their molecular hyperpolarizability is not unusually large [4]. Since then, many organometallic molecules have been studied, some of which exhibit extremely large hyperpolarizabilities [2,5–7]. In particular, a promising class of  $\eta^5$ -cyclopentadienyl complexes of the type  $[\text{MCp}(\text{P}_\text{P})(\text{NC}-\pi\text{-X})]$  (where M = metal, Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>, P<sub>P</sub> = bidentate phosphine ligand,  $\pi$  = conjugated chain, and X = electron donor or acceptor) has been developed [8,9], and we studied the NLO properties in a systematic series, varying the metal ion (M = Co, Ni, Ru, Fe) [10], as well as the conjugated chain and the phosphine coligand [11]. These studies showed that the organometallic fragment  $[\text{MCp}(\text{P}_\text{P})]^+$  acts as a very efficient electron  $\pi$  donor when M = Fe (leading to  $\sim 4$  times higher  $\beta$  than with Ru), and yields high hyperpolarizabilities when combined with an acceptor group (X = NO<sub>2</sub>) to form a push–pull system.

As a result,  $\beta$ -values up to  $395 \times 10^{-30}$  esu were measured in chloroform solution for such a Fe(II) compound with a short conjugated ligand *p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, taking DPPE (= 1,2-bis(diphenylphosphino)ethane) as electron-rich phosphine group [10]. This value went up to  $570 \times 10^{-30}$  esu upon increase of the conjugation length of the ligand using *p*-C(H)=C(H)C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> [11]. The change from (+)-DIOP to DPPE had a positive but rather marginal effect on  $\beta$ , which leaves open the possibility of engineering the phosphine ligand for other purposes, e.g., influencing the molecular arrangement.

Unfortunately, high molecular hyperpolarizabilities and well aligned crystal packing tend to exclude each other, because the large dipole moments typically associated with push–pull systems

tend to favor anti-parallel alignment of neighboring molecules, thus cancelling out their second-order NLO responses. One of the strategies proposed to overcome this problem is to use octupolar molecules [12,13]. Alternatively, ionic salts of push–pull chromophores have been suggested as second-order NLO crystals [14]. These salts are more likely to form noncentrosymmetric crystals because the Coulomb interaction with the counterions can override the detrimental dipole–dipole interactions. The separation and shielding provided by the counterions also reduces the dipole–dipole interactions between the chromophores. This has led to the design of organic salt crystals with a perfect [15,16] or nearly perfect (e.g., DAST [14,17]) alignment of the chromophores. Many more efforts have been put into designing organic dye crystals with a favorable orientation, e.g., by making use of specific interactions such as hydrogen bonding between chromophores [18,19], but crystals with a perfect chromophore alignment are still very rare. To the present day, DAST is probably still the most well-known organic NLO crystal and, to our knowledge, the only commercially available organic dye crystal for NLO applications.

We report here the characterization of second-order NLO and crystallographic properties of an ionic compound, the complex  $[\text{FeCp}((\text{R})\text{-PROPHOS})(\text{p-NCC}_6\text{H}_4\text{NO}_2)][\text{PF}_6]$ , with a chiral bidentate phosphine ligand (R)–PROPHOS. A high value of the hyperpolarizability is found to be combined in this compound with a perfectly aligned crystal packing, which is expected to lead to a high NLO susceptibility of the crystal. We will further examine the factors leading to the particular crystal structure with P1 space group.

## 2. Experimental

Details of the synthesis of the complex  $[\text{FeCp}((\text{R})\text{-PROPHOS})(\text{p-NCC}_6\text{H}_4\text{NO}_2)][\text{PF}_6]$  have been reported elsewhere [11]. Crystals suitable for X-ray studies were grown by diffusion of diethyl ether into a dichloromethane solution of the complex.

Hyper-Rayleigh scattering (HRS) [20,21] measurements were performed in CHCl<sub>3</sub> solution

(concentrations in the order of  $5 \times 10^{-5}$  mol/l) at a fundamental wavelength of 1064 nm using a Nd:YAG regenerative amplifier, and a detection scheme that eliminates any erroneous contributions from multi-photon excited fluorescence by spectral and temporal analysis of the scattered light. The measurements were calibrated against chloroform ( $|\beta_{zzz}(\text{CHCl}_3)| = 0.49 \times 10^{-30}$  esu) [22]. Details of the set-up and data analysis have been described before [2,10]. No significant fluorescence background was present for this compound.

X-ray diffraction data were collected at 293(2) K on an Enraf–Nonius MACH3 diffractometer, using MoK $\alpha$  radiation ( $\lambda(\text{Mo–K}\alpha) = 0.71069$  Å). Crystal data:  $[\text{C}_{39}\text{H}_{35}\text{F}_6\text{FeN}_2\text{O}_2\text{P}_3 \cdot \text{CH}_2\text{Cl}_2]$ ,  $M_r$  911.38, triclinic, space group  $P1$ ,  $a = 10.413$  Å,  $b = 10.669(2)$  Å,  $c = 10.684(2)$  Å,  $\alpha = 69.74(1)^\circ$ ,  $\beta = 67.15(1)^\circ$ ,  $\gamma = 82.60(2)^\circ$ ,  $V = 1026.1(3)$  Å<sup>3</sup>,  $D_{\text{calc}} = 1.475$  Mg m<sup>-3</sup>,  $Z = 1$ ,  $\mu(\text{Mo–K}\alpha) = 0.679$  mm<sup>-1</sup>. Using the CAD4 software, data were corrected for Lorentz and polarization effects and empirically for absorption. Intensities of 3579 unique reflexions in the range  $2.03 < \theta < 26.97^\circ$  were measured by the  $\omega - 2\theta$  scan mode. The structure was solved with SHELXS-97 [23] and refined by the full-matrix least-squares method with SHELXL-97 [24], included in OSCAIL Version 8 [25]. 2641 reflections with  $I > 2\sigma(I)$  were used in the structure solution and refinement. Final  $R_1$ ,  $wR_2$  and goodness of fit(s) were 0.078, 0.195 and 1.15, respectively, for 505 refined parameters.

Nonhydrogen atoms were anisotropically refined and all hydrogen atoms were inserted in calculated positions and refined isotropically riding with the parent carbon atom. The illustrations were drawn with programs ORTEP-II [26] included in OSCAIL Version 8 and SCHAKAL [27], and Accelrys ViewerLite 4.2. The atomic scattering factors and anomalous scattering terms were taken from *International Tables* [28]. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC) No. CCDC188050. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

### 3. Results and discussion

The complex  $[\text{FeCp}(\text{R})\text{–PROPHOS}(\textit{p}\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{PF}_6]$  was found to possess a large first hyperpolarizability,  $|\beta_{zzz}| = 545 \times 10^{-30}$  esu, as expected from our previous studies of similar complexes [10,11]. In fact, this value is significantly larger than that of the analogous compound with a DPPE phosphine ligand, even though the structural difference is very small and we showed previously that in most cases the phosphine ligand has only modest effects on  $\beta$ . This increase in  $\beta$  can be explained by a slight increase in the donor strength of the organometallic moiety, which also red-shifts the charge-transfer transition and thus increases the near-resonance enhancement of  $\beta$ .

The molecular diagram of the cation  $[\text{FeCp}(\text{R})\text{–PROPHOS}(\textit{p}\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)]^+$  is shown in Fig. 1, along with the atom numbering scheme. The structural study confirms the presence of the  $\text{PF}_6^-$  anion and reveals the presence of one crystallization solvent (dichloromethane) molecule (see Fig. 2).

The metal is coordinated to the  $\eta^5$ -cyclopentadienyl ring, two phosphorus atoms of the phosphine ligand and to the nitrile nitrogen atom of the  $\textit{p}\text{-NCC}_6\text{H}_4\text{NO}_2$  ligand. The coordination geometry is pseudo-octahedral (three-legged piano stool), on the assumption that the cyclopentadienyl group takes up three coordination sites. The chelating phosphine displays the expected R configuration at C(131) (absolute structure parameter, 0.01(4)). The overall coordination geometry as well as the bond distances and angles within the benzonitrile group are very similar to the other iron(II)monocyclopentadienyl derivatives containing DPPE and nitrile bonded ligands [11,29]. Distances and angles within the benzonitrile group, in particular the absence of any obvious bond length alternation, are consistent with the retention of aromaticity. Apparently, the quinoidal character expected to be induced by the  $\pi$  back-donation, which is suggested by the spectroscopic IR and NMR data obtained for the complex [11], is too small to be observed in the X-ray crystal structure.

The most remarkable property of this compound is that it not only has a large hyperpolarizability, but

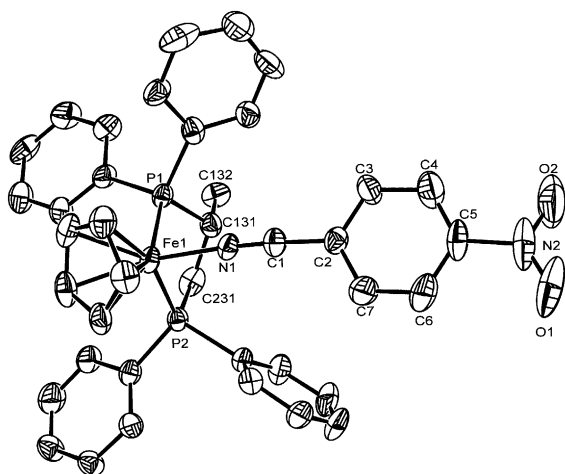


Fig. 1. ORTEP diagram for  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)((\text{R})\text{-PROPHOS})(p\text{-N}\equiv\text{CC}_6\text{H}_4\text{NO}_2)][\text{PF}_6]$ , with 50% thermal ellipsoids, showing the labeling scheme. The hydrogen atoms were omitted for clarity. Selected distances and angles: Fe1–N1 (1.902(9) Å); Fe1–N1–C1 (172.0(10)°); N1–C1–C2 (172.8(13)°); Fe1–P1 (2.211(3) Å); Fe1–P2 (2.219(3) Å); P1–Fe1–P2 (86.2(1) Å).

that it also exhibits a noncentrosymmetric crystal packing (triclinic space group P1) with only a single chromophore in the unit cell, which implies that all the dipolar chromophores are perfectly parallel. To our knowledge, this is the first report of an organometallic compound with such a large hyperpolarizability that shows this ideal crystal packing maximizing the macroscopic second-order NLO susceptibility.

To understand why this compound yields a perfectly aligned crystal packing, despite the well known tendency for dipolar chromophores to pack in an antiparallel way, we will now examine the crystal structure depicted in Figs. 2 and 3. First we consider the stabilization by attractive Coulomb interactions. The charges relevant to this are the  $-e$  charge of the counterion, and the ones localized on the donor and acceptor groups of the chromophores, with a  $(+1 + \delta)e$  charge on the iron ion, and  $-\delta e$  charge on the  $\text{NO}_2$  donor group. The spatial arrangement of charges is shown in

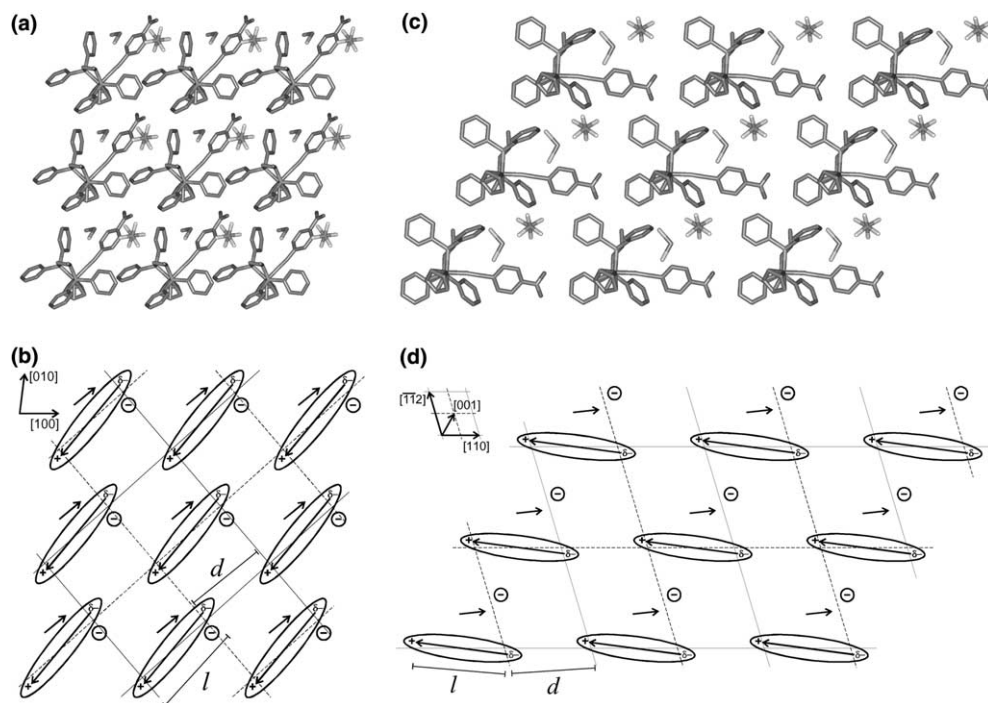


Fig. 2. Crystal packing. (a) and (b) show a section of a (001) plane ( $ab$  plane), and (c) and (d) a section of the  $(1\bar{1}0)$  plane. The schematic diagrams illustrate the arrangement of dipoles and charges, as well as the nonprimitive (face centered) lattice described in the text. For clarity, hydrogen atoms are not shown, and the  $(1 + \delta)+$  charge of the organometallic fragment is abbreviated to '+'. For clarity, hydrogen atoms are not shown, and the  $(1 + \delta)+$  charge of the organometallic fragment is abbreviated to '+'. Dimensions  $l$  and  $d$  are indicated in (b) and (d).

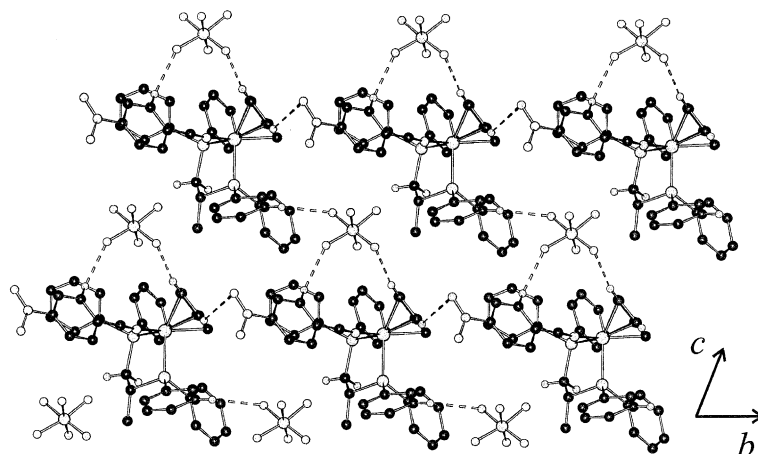


Fig. 3. Packing along  $a$  showing the short hydrogen bonding that hold together anions and cations. The 1D alignment (along  $b$ ) due to the C–H $\cdots$ O is also indicated.

Figs. 2b, d for two sections of the crystal, in which also the molecular units and their dipole moments are symbolically indicated.

The (001) section (see Figs. 2a, b) consist of a layer of chromophores (approximately oriented along [110]), with part of the phosphine ligands sticking out of the layer and the counterions and solvent molecules filling the remaining channels along the [100] direction between these phosphine ligands. In this plane one observes an energetically favorable arrangement of alternating charges on a near-to-square grid (emphasized by the full and broken lines), similar to that in a {100} plane of a NaCl-type ionic crystal (to make the analogy with the face-centered NaCl structure one can define an alternative, nonprimitive lattice  $[\vec{a}', \vec{b}', \vec{c}']$  as  $\vec{a}' = \vec{a} - \vec{b}$ ,  $\vec{b}' = \vec{a} + \vec{b}$  and  $\vec{c}' = 2\vec{c} - \vec{a} - \vec{b}$ , which gives  $a' = 13.91 \text{ \AA}$ ,  $b' = 15.84 \text{ \AA}$ ,  $c' = 19.41 \text{ \AA}$ ,  $\alpha' = 106.15^\circ$ ,  $\beta' = 87.27^\circ$ , and  $\gamma' = 91.40^\circ$ ). While this explains the stability of Coulomb interactions within the (001) planes, the stacking of these (001) planes into a stable three-dimensional crystal structure can be understood by noting that these overall positively charged layers of chromophores are alternated with layers of negatively charged counterions and solvent molecules. The (001) planes are stacked with the positively charged organometallic group of one layer between the nitro acceptor groups of the previous

layer and the  $\text{PF}_6^-$  anions of the next layer, as can be seen in a section of a (110) plane (Figs. 2c, d), which is close to perpendicular ( $\beta' = 87.27^\circ$ ) to the (001) planes. An additional stabilization is provided by the solvent molecules which have a dipole moment oriented antiparallel to that of the chromophores.

Thus, this alternating arrangement of charges is expected to provide the necessary stabilization of Coulomb interactions in the aligned crystal structure. It is important to note that in order for such a NaCl like structure to be realized, the distance  $d$  between the dipoles within the chains of dipoles arranged head-to-tail along the  $b'$  direction needs to be approximately the same as the length  $l$  of the dipoles (see Fig. 2),  $d \cong l$ , otherwise, it would be energetically more favorable for these chains to be arranged in alternating orientations. Indeed, taking the Fe atom and the nitro group's N atom (N2) as the end points of the dipolar chromophore, these distances are very close for the present structure ( $d = 7.54 \text{ \AA}$  and  $l = 8.61 \text{ \AA}$ ), thanks to the spacing provided mostly by two of the phenyl rings of the phosphine ligand that extend beyond the metal end of the dipole (and to some extent also by a phenyl ring of another neighboring molecule; see Fig. 2a).

Based on these general considerations however, a similar NaCl-like crystal structure in which al-

ternating chains of dipolar chromophores have an *opposite* orientation would result in the same alternating arrangement of charges and thus remains equally possible. Other aspects such as slight specific interactions (e.g., hydrogen bonding and sterical hindrance) will then decide which structure will be formed. The inclusion of a chiral center (in the chiral phosphine ligand (R)-PROPHOS) increases the chances of forming a favorable structure by excluding all centrosymmetric space groups [8,30]. Indeed, the analogous compound with the nonchiral phosphine ligand DPPE was found to form centrosymmetric crystals [11].

To show the specific interactions that can also contribute to the stabilization of the structure with perfectly aligned molecular dipoles, the intermolecular contacts are visualized in a view of the structure along the [1 0 0] direction (Fig. 3). The crystal packing is stabilized by C–H...F (in the range 2.425–2.502 Å) and C–H...O hydrogen interactions. Each PF<sub>6</sub><sup>-</sup> holds together two cationic molecules from different layers, through the interactions of C–H(14)...F(3) and C–H(7)...F(6) from one molecule and a C–H(113)...F(5) interaction with another cationic molecule.

The supramolecular alignment of the molecules is also reinforced by two charge assisted and independent C–H...O hydrogen bonding interactions. One bond (2.855 Å) between the O(1) atom of the nitro group and a hydrogen of the Cp ring of a neighbor cation molecule in the same layer, extends the 1D alignment along the *b* crystallographic direction. The second hydrogen interaction (2.852 Å; not visible in Fig. 3), between oxygen O(2) and a phosphine aromatic hydrogen belonging to a cationic molecule from a neighboring layer, connects the cation molecules along the *a* axis and is also responsible for the overall alignment in the lattice. Very similar considerations, both regarding the Coulomb interactions and the hydrogen bonding also apply to the structure of a related chiral Ru complex, except for the presence of the solvent molecule in the present compound [30].

The combination of the large molecular hyperpolarizability and a perfectly aligned crystal structure is expected to lead to an unusually large macroscopic nonlinear susceptibility, which in that case is given by [1]

$$\chi_{ijkl}^{(2)} = N f_j f_k f_l \beta_{ijkl},$$

where  $N$  is the number density of molecules ( $N = 9.747 \times 10^{26} \text{ m}^{-3}$  from the X-ray data), and  $f_i$  are the local field factors for the respective polarization directions and frequencies involved. For comparison, even the well-known organic NLO crystal DAST [14,17] has a molecular hyperpolarizability of only  $69 \times 10^{-30} \text{ esu}$  (at 1542 nm) in the solid state, compared to  $367 \times 10^{-30} \text{ esu}$  in solution (measured at 1542 nm to avoid fluorescence contributions) [31]. DAST has an only approximately parallel alignment of the chromophores in the crystal structure, but has almost twice the number density of the present organometallic complex ( $N_{\text{DAST}} = 1.906 \times 10^{27} \text{ m}^{-3}$ ). For the present compound, the local field factors for the crystalline state as well as any changes of the molecular  $\beta$  possibly induced by the crystalline environment, are not known. Considering that the intramolecular interactions in the crystal are mostly attractive Coulomb interactions, it seems plausible that the effect of the crystalline environment would be similar to that of a polar solvent, and would increase the charge-separation. Given the positive solvatochromism of this type of compounds [11] (e.g., absorption maximum of the present compound in chloroform: 475 nm; in dimethylsulfoxide: 498 nm), and the observation from the X-ray data that the phenyl ring of the conjugated ligand is still essentially aromatic, we anticipate on the basis of the bond length alternation (BLA) model [32] that the molecule resides in the far left-hand side of the BLA diagram (in contrast with the merocyanine dyes such as DAST) where  $\beta$  still increases with increasing environment polarity. Thus, a macroscopic nonlinearity several times larger than that of DAST may be anticipated. Further study is required to assess the actual solid state NLO susceptibility, and its dispersion. In particular, for applications it is also important to know the angle between the charge transfer axis of the NLO chromophores and the optical axes.

In order for the crystal to be useful for electro-optical applications, transparency in the near IR is also essential. The solid state optical absorption spectrum of the compound was assessed by diffuse

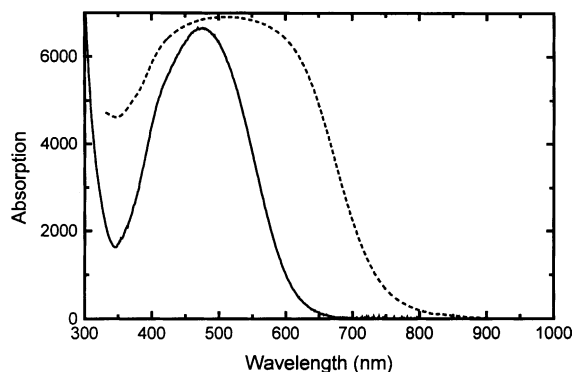


Fig. 4. Absorption spectrum of the compound in  $\text{CHCl}_3$  solution [solid line; extinction coefficient in  $l/(\text{mol cm})$ ] and solid state absorption spectrum (dashed; arbitrary absorbance units) obtained by diffuse reflectance spectroscopy.

reflectance spectroscopy (see Fig. 4), and was found to be comparable to the solution spectrum, but redshifted. This suggests that the molecules retain their optical properties in the solid state. The red-shift is in agreement with the above considerations on BLA and with the observed positive solvatochromism. The material is thus transparent at NIR diode laser wavelengths starting above  $\sim 800$  nm, and in the telecom range as well.

#### 4. Conclusions

The organometallic compound  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)((\text{R})\text{-PROPHOS})(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{PF}_6]$  was shown to possess a large first hyperpolarizability and furthermore to form a crystal structure with the desired perfect alignment of the NLO chromophores, which is promising for high macroscopic nonlinearities. An analysis of the crystal structure has revealed several aspects that can be important to the design of other second-order NLO crystalline materials. The molecular alignment in this ionic crystal is favored by the inclusion of chiral groups and by hydrogen bonding. The inclusion of spacer groups beyond the end of the dipolar chromophore, which provides a spacing equal to the length of the chromophore, is considered as a further element in the electrostatic stabilization of the polar ordering.

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