

# Role of Donor-Acceptor Orientation on Solvent-Dependent Three-Photon Activity in Through-Space Charge-Transfer Systems - Case Study of [2,2]-Paracyclophane Derivatives

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## Abstract

We study the effect of donor-acceptor orientation on solvent-dependent three-photon transition probabilities ( $\delta^{3PA}$ ) of representative through-space charge-transfer (TSCT) systems - namely, doubly positively charged [2, 2]-paracyclophane derivatives. Our cubic response calculations reveal that the value of  $\delta^{3PA}$  may be as high as  $10^6$  a.u., which can further be increased by a specific orientation of the donor-acceptor moieties. To explain the origin of the solvent cum orientation dependency of  $\delta^{3PA}$ , we have calculated different three-photon tensor components using a two-state model, noting that only a few tensor elements contribute significantly to the overall  $\delta^{3PA}$  value. We show that this dependence is due to the large dipole moment difference between the ground and excited states of the systems. The dominance of a few tensor elements indicates a synergistic involvement of  $\pi$ -conjugation and TSCT for the large  $\delta^{3PA}$  of these systems.

# 1 Introduction

The need for highly sensitive experimental set-ups and the computational costs has made the study of multi-photon absorption (MPA) processes a challenging task. In addition to the experimental and computational obstacles, one obvious problem of MPA processes is that their transition probabilities are found to decrease with increasing order of the MPA processes. Because of these limitations, very few processes beyond the lowest-order MPA process, two-photon absorption (2PA),<sup>1-13</sup> have been extensively studied, theoretically as well as experimentally. MPA processes are characterized by the high spatial confinement of the excitations and the use of long wavelength radiation, relying on the non-linear relation between the transition probabilities and the intensity of the incident radiation and arising because of the involvement of intermediate virtual states in the excitation process. The higher the order of the MPA process, the more tangible these qualities of the MPA processes are expected to be.<sup>14-17</sup> The improved sensitivity of the higher-order MPA processes over 2PA have raised expectations in technologically advanced fields. However, the experimental measurement of MPA cross-sections is always a difficult task, even for a 2PA process, because of their dependence on many factors such as sample purity, spatial and temporal fluctuations and also because MPA occurs very close to the material damage threshold. In addition to this, MPA is further complicated by the dependence of the process on the polarization of the light and its orientation relative to the crystal axis and the existence of many possible intermediate states. In spite of all these difficulties, some theoretical and experimental works have in recent past been devoted to the study of higher-order MPA processes, mainly the three-photon absorption (3PA) process. He et al.<sup>14</sup> have shown that 3PA can be used in frequency upconversion lasing, short-pulse optical communications and the measured<sup>15</sup> 3PA cross-section for a thiophene

derivative in THF solvent was found to be  $8.8 \times 10^{-76} \text{ cm}^6 \text{ s}^2$ . Maiti et al.<sup>16</sup> have applied the 3PA technique in the field of bio-imaging of the tryptophan and serotonin molecules. Similarly, the applications<sup>18-21</sup> of 3PA in optical limiting, short-pulse fiber communication and light-activated therapy have been demonstrated by different research groups. From a theoretical point of view, efficient theoretical/computational studies of the 3PA process of realistic systems has become possible with the implementation of cubic response (CR)<sup>29</sup> theory in the framework of time-dependent density functional theory (TDDFT).<sup>30,31</sup> Using this approach, Cronstrand et al.<sup>22-24</sup> and Safek et al.<sup>25</sup> have theoretically studied some larger molecular systems. Lin et al.<sup>26</sup> studied the effect of a solvent on the 3PA of symmetric charge-transfer molecules. As the full sum-over-states calculations are computationally very expensive, few-state models have recently been used for studying the 3PA process, but unlike the case of 2PA, a noticeable random divergence has been reported in this case. With this introductory background, it can be argued that the study of real-life 3PA applications using the hitherto existing theoretical models is limited to the calculation of 3P transition probabilities/cross-sections and is still at an early stage. In order to have a proper control of the 3PA activity of a system, several facets of this field need proper exploration.

As seen for the TPA process,<sup>32-34</sup> the orientation of donor-acceptor groups in a system could have profound impact on the 3PA process. In the present work, our aim is to unravel the mechanisms of the 3PA process by studying the effect of donor-acceptor orientation and that of the solvent, on a hitherto unexplored class of molecules, namely a through-space charge-transfer (TSCT) system. For this purpose, we have chosen three doubly positively charged [2,2]-paracyclophane derivatives having different orientations of the donor-acceptor moieties. The three-photon (3P) transition probabilities and other required parameters of the first two excited states of all these systems in gas phase and in two different solvents (MeCN and tetrahydrofuran (THF)) are calculated using CR theory as implemented within TDDFT.<sup>29</sup> Solvent-phase CR calculations have been performed using the Polarizable Continuum Model (PCM).<sup>35</sup> Furthermore, the origin of this solvent cum orientation dependency have been

explained using two-state model (2SM) calculations in both the gas as well as in different solvent phases.

## 2 Computational Details

Geometries of the PCP1 molecule (see Figure 1) in gas phase and in two different solvents (MeCN and THF) have been taken from our previous work<sup>4</sup> where the optimization was done at the B3LYP/6-311G (d,p) level of theory. The other two molecules were optimized at the same level of theory using the Gaussian 03 suite of programs,<sup>36</sup> the solvent effects in all cases described by the PCM.<sup>37</sup> With these optimized geometries we have calculated, from the residues of TDDFT-based CR functions, the 3PA parameters for the transition from the ground to the first excited state of all systems both in the gas as well as in the two solvent phases. These calculations were performed using the CAMB3LYP<sup>38</sup> functional and Dunning's cc-pVDZ basis set.<sup>39</sup> This combination of exchange-correlation functional and basis set has been shown to work accurately in the case of the TPA of intramolecular charge-transfer molecules<sup>6,40</sup> and we expect it to perform well in the study of 3PA as well. For the solvent-phase calculations, the non-equilibrium formulation<sup>35</sup> of CR theory within PCM has been used and all the response calculations have been performed using the DALTON program package.<sup>41</sup> Considering the huge computational cost for calculating the 3PA transition probabilities of the systems in the solvent, we restrict this study to two solvents only, one polar (MeCN) and another of intermediate polarity (THF). After the response theory calculations, we have reevaluated the 3PA parameters using a two-state model approach.

## 3 Results and discussion

The systems studied in this contribution are shown in Fig. 1. We will refer to these molecules as PCP1, PCP2 and PCP3, respectively. In all molecules,  $-NMe_2$  and  $-NMe_3^+$  are respectively the donor and acceptor groups. The two donor groups are attached to one of the benzene rings and the two acceptors are attached to the second benzene ring of the systems. This particular configuration favors the TSCT

nature of the system. In PCP1, the donor moieties are placed at the (2, 5) positions whereas the acceptor moieties are located at the (3', 6') positions of the two rings. Similarly, in PCP2 and PCP3 the donor groups are placed at (3, 6) and (2, 6) positions and acceptors at (3', 6') and (3', 5') positions respectively. For clarity, the atom-labeling is also shown in Fig. 1. Furthermore, to make the discussion easier, the orientation of the donor and acceptor groups in PCP1 will be marked by “x”. In PCP2, the orientation of the donors and acceptors can be represented by “=”, indicating that both donor moieties are placed on one benzene ring, while the acceptors are attached to the other ring. Finally, PCP3 can be symbolized by “X” and here the upper part of “X” represents the donors and the lower part the acceptors.

We first consider the one-photon absorption (OPA) process in the three systems. The OPA data as obtained using linear response theory for the first excited state of all three systems in both the gas as well as in different solvent phases are reported in Table 1. From the table, we note that the first excited state of all three molecules is weakly OPA active in both of the two solvents as well as in gas phase. The oscillator strength ( $\delta_{\text{OPA}}$ ), which determines the strength of the one-photon transition in a system, is directly proportional to the product of the ground- to excited-state transition energy and the square of the corresponding transition dipole moment vector ( $\mu^{0f}$ ). It is obvious from Table 1 that both of these quantities (in a.u.) have very small values for all the three molecules in both the gas as well as in the different solvent phases, making their  $\delta_{\text{OPA}}$  very small and thus the excitation is only weakly OPA active. These results are also consistent with our previous work<sup>4</sup> on the one- and two-photon absorption of PCP1. We have already rationalized the long-range nature of the  $S_0$ - $S_1$  transition for PCP1 in our previous work. Similar to that study, we have here computed the contributions of different orbitals involved in the  $S_0$ - $S_1$  transition of the three molecules and the results are given in Table 1. The results clearly show that irrespective of the nature of the solvent, the dominant contribution to the  $S_0$ - $S_1$  transition comes from the HOMO-LUMO orbital pairs for all molecules. These orbitals are depicted in Figs. 2, 3 and 4 for the three molecules, and clearly show that the HOMO is mainly located on the donor

side of the molecules whereas the LUMO is localized on the acceptor side. This reveals the TSCT nature of the  $S_0$ - $S_1$  transition in all these molecules in both the gas as well as in different solvent phases. In order to understand the nature of this transition in more detail, we have plotted the differential electron density plot between the HOMO-LUMO orbital pair for all three molecules. These plots are generated by subtracting the Gaussian cube files containing the HOMO and LUMO electron densities (isovalue = 0.06) and are collected in Figs. 2, 3 and 4. It is obvious from the plots that, for both PCP1 and PCP2, no changes occur on moving from either the gas phase to the solvent phase or from one solvent to another. In contrast, PCP3 shows significant changes in the differential electron density mapping in the gas and solvent phases. These changes are observed only in the electron density of the donor group containing the benzene ring, where one of the  $-NMe_2$  is not participating in the TSCT process in the solvent phases. To further clarify the nature of the  $S_0$ - $S_1$  transition, we have computed the  $\Lambda$  parameter,<sup>42,43</sup> which can quantify the long-/short-range nature of a transition. It may have values between 0 and 1, and the long-range nature of a transition is identified by a small value of  $\Lambda$ , indicating small orbital overlap. The results are given in Table 1. From these data, we see that irrespective of the nature of the solvent, the value of  $\Lambda$  for all three molecules is very small (around 0.2), which clearly indicates that the  $S_0$ - $S_1$  transition in all these molecules is truly of long-range nature. We note that although the validity of DFT for studying TSCT transitions may be questioned, the reliability of the CAMB3LYP functional for TSCT transitions has been verified against CC2 calculations for transitions of the same kind as those studied here.<sup>44</sup>

After the above OPA discussion, we now move to the 3PA process in the three molecules. However, before discussing our results, let us briefly outline the theoretical basis for our calculations. Being related to the fifth-order susceptibility, the three-photon transition probability ( $\delta^{3PA}$ ) is a challenge for *ab initio* calculations. The  $\delta^{3PA}$  of a system can be expressed in a simple manner in terms of 3P transition tensor elements ( $T_{ijk}$ ), and for linearly polarized light this relation can be written as<sup>45</sup>

$$\delta^{3PA} = \frac{1}{35} \sum_{i,j,k} (2T_{ij}T_{kkj} + 3T_{ijk}^2) \quad (1)$$

Where, the factor (1/35) arises because of orientational averaging. The  $T_{ijk}$  terms appearing in Eq.1 can be obtained from the single residue of the CR function. Alternatively, for a resonant absorption,  $T_{ijk}$  can be expressed in terms of different components of third-order transition dipole moment vectors and the corresponding transition energies and these can easily be extracted from the residues and poles of linear ( $\langle 0|\mu_i|n\rangle$ ) or quadratic ( $\langle n|\mu_i|m\rangle$ ) response functions. The relationship between  $T_{ijk}$ , different transition moments and excitation energies is given by

$$T_{ijk} = \sum p_{ijk} \sum_{m,n} \frac{\langle 0|\mu_i|m\rangle \langle m|\mu_j|n\rangle \langle n|\mu_k|f\rangle}{(\omega_m - \omega_f/3)(\omega_n - 2\omega_f/3)} = \sum p_{ijk} \sum_{m,n} \frac{\mu_i^{0m} \mu_j^{mn} \mu_k^{nf}}{(\omega_m - \omega_f/3)(\omega_n - 2\omega_f/3)} \quad (2)$$

where,  $\mu_i^{\alpha\beta} = \langle \alpha|\mu_i|\beta\rangle$  is the  $i^{\text{th}}$  component of the transition dipole moment vector for a transition from the  $\alpha^{\text{th}}$  state to the  $\beta^{\text{th}}$  state,  $\omega_\alpha$  is the transition energy from the ground to the  $\alpha^{\text{th}}$  state, and  $\sum p_{ijk}$  represents the summation over all the permutations of indices i, j and k which runs over the Cartesian coordinates x, y and z.

With this brief theoretical background, we now turn to the results of our 3PA study. The values of  $\delta^{3PA}$  for the first excited state of all the three systems in gas as well as in different solvent phases, along with the different three-photon tensor elements  $T_{ijk}$  are reported in Table 2. The data in Table 2 clearly indicate that irrespective of the nature of the solvent, all three systems have large  $\delta^{3PA}$  values ( $\geq 10^6$  a.u.). At the same time, all these molecules are consistently more 3PA active in gas phase as compared to the solvent phase. The  $\delta^{3PA}$  in the less polar solvent, THF, are always larger than that in the more polar MeCN solvent. Exactly the same solvent dependence for the two-photon transition probability of PCP1 was observed in our previous study.<sup>4</sup> This is not surprising since the basic mechanisms of both the 2PA and 3PA processes are very similar and hence can be expected to be affected in a similar manner by different solvents. The results also show that in the gas phase, PCP3 have much larger  $\delta^{3PA}$  values



than the other two molecules. The value of gas phase  $\delta^{3PA}$  for PCP3 is indeed the largest value obtained in this work. When going from gas phase to solvent phase, PCP3 becomes much less 3PA active than both PCP1 and PCP2.

To understand the origin of this orientation cum solvent-dependent 3PA activity of the three systems, we can inspect the relative contributions of the different 3PA tensor elements ( $T_{ijk}$ ). These are supplied in Table 2, and shows that the largest contributions in the “x” orientation (PCP1) are  $T_{yyx}$  and  $T_{yyz}$  both in the gas and solvent phases. Similarly, in the “=” orientation (PCP2), the largest contributions come from  $T_{xxx}$ ,  $T_{yyy}$ ,  $T_{yyx}$  and  $T_{yyz}$ . However, in case of the “X” orientation (PCP3), unlike the other two molecules, most of the  $T_{ijk}$  terms contribute significantly to the overall  $\delta^{3PA}$  values. It is important to note that if we divide the molecules in two parts (by cutting perpendicular to the C2-C3 and C6-C5 bonds, see Fig. 1) then in both the “x” and “=” orientation the two parts will have both donors and acceptors, but in the “X” orientation, one part will have only the two donor groups whereas the other part will have two acceptor groups. This characteristic distinguishes PCP3 from the other two systems and is probably the origin of the large solvent dependency of its 3PA activity.

In order to understand the dominance of the selective  $T_{ijk}$  terms and the effect of donor-acceptor orientation, we have considered the sum-over-states expression of the 3PA transition probability in Eq. 2. Although Eq.2 contains easily understandable quantities, the analysis of the expression is made difficult by the large number of intermediate states that appear in the summations. To get insight into the qualitative origin of the 3PA process of the systems, we have simplified Eq. 2 by using a two-state model (2SM) approach involving only the ground ( $S_0$ ) and the first excited states ( $S_1$ ). Unlike 2PA, the expression for the tensor elements involved in the 3PA process is still complicated. Within the 2SM, after expanding Eq. (2), each  $T_{ijk}$  will have 19 terms, given by

$$\begin{aligned}
T_{ijk} = & \frac{9}{2\omega_f^2} \left[ \mu_i^{00} \mu_j^{00} \mu_k^{0f} + \mu_i^{00} \mu_k^{00} \mu_j^{0f} + \mu_j^{00} \mu_i^{00} \mu_k^{0f} + \mu_j^{00} \mu_k^{00} \mu_i^{0f} + \mu_k^{00} \mu_i^{00} \mu_j^{0f} + \mu_k^{00} \mu_j^{00} \mu_i^{0f} \right] \\
& - \frac{9}{\omega_f^2} \left[ \mu_i^{00} \mu_j^{0f} \mu_k^{ff} + \mu_i^{00} \mu_k^{0f} \mu_j^{ff} + \mu_j^{00} \mu_i^{0f} \mu_k^{ff} + \mu_j^{00} \mu_k^{0f} \mu_i^{ff} + \mu_k^{00} \mu_i^{0f} \mu_j^{ff} + \mu_k^{00} \mu_j^{0f} \mu_i^{ff} \right] \\
& + \frac{9}{2\omega_f^2} \left[ \mu_i^{0f} \mu_j^{ff} \mu_k^{ff} + \mu_i^{0f} \mu_k^{ff} \mu_j^{ff} + \mu_j^{0f} \mu_i^{ff} \mu_k^{ff} + \mu_j^{0f} \mu_k^{ff} \mu_i^{ff} + \mu_k^{0f} \mu_i^{ff} \mu_j^{ff} + \mu_k^{0f} \mu_j^{ff} \mu_i^{ff} \right] \\
& - \frac{27 \mu_i^{0f} \mu_j^{0f} \mu_k^{0f}}{2\omega_f^2}
\end{aligned} \tag{3a}$$

This equation can be reduced to a simpler form using  $\Delta\mu_i^{ff}$  to indicate the difference in dipole moment between the excited and ground states of the molecule

$$T_{ijk} = \frac{9}{2\omega_f^2} \left[ \Delta\mu_i^{ff} \Delta\mu_j^{ff} \mu_k^{0f} + \Delta\mu_i^{ff} \Delta\mu_k^{ff} \mu_j^{0f} + \Delta\mu_j^{ff} \Delta\mu_i^{ff} \mu_k^{0f} + \Delta\mu_j^{ff} \Delta\mu_k^{ff} \mu_i^{0f} \right. \\
\left. + \Delta\mu_k^{ff} \Delta\mu_i^{ff} \mu_j^{0f} + \Delta\mu_k^{ff} \Delta\mu_j^{ff} \mu_i^{0f} - 3\mu_i^{0f} \mu_j^{0f} \mu_k^{0f} \right] \tag{3b}$$

and finally

$$T_{ijk} = \frac{9}{2\omega_f^2} \left[ 2(\Delta\mu_i^{ff} \Delta\mu_j^{ff} \mu_k^{0f} + \Delta\mu_i^{ff} \Delta\mu_k^{ff} \mu_j^{0f} + \Delta\mu_j^{ff} \Delta\mu_k^{ff} \mu_i^{0f}) - 3\mu_i^{0f} \mu_j^{0f} \mu_k^{0f} \right] \tag{3c}$$

Eq.3c shows that the values of the different  $T_{ijk}$  within the 2SM depend on  $\omega_f$  and the different components of  $\Delta\mu^{ff}$  and  $\mu^{0f}$ . It is also apparent from this equation that large positive values of different components of  $\Delta\mu^{ff}$  and a concomitant small value of  $\omega_f$  will ensure a large value of the corresponding  $T_{ijk}$ . It must also be noted that large positive values of different components of  $\mu^{0f}$  decrease the overall  $T_{ijk}$  because of the last term in equation 3c. However, in the calculations one must keep in mind that the overall values of different  $T_{ijk}$  strongly depend on both the magnitude as well as on the sign of the three components of  $\Delta\mu^{ff}$  and  $\mu^{0f}$ . From Table 1, it can be noted that the magnitude of  $\Delta\mu^{ff}$  is much larger (more than 75 times, e.g. for PCP3 in MeCN solvent) than that of  $\mu^{0f}$  for all the systems in both the gas and solvent phases. For PCP1 and PCP2, the  $x$  and  $z$  components of  $\Delta\mu^{ff}$  are very small compared to its  $y$  component. In PCP1, the  $y$  component of  $\mu^{0f}$  is zero, and for this reason, all terms except  $T_{yyx}$  and  $T_{yyz}$  are very small for this system in the gas phase. The large contribution of  $T_{yyx}$  and  $T_{yyz}$  in PCP2 can be explained in a similar way. In PCP3, all the components of  $\Delta\mu^{ff}$  and  $\mu^{0f}$  are much higher than in PCP1

and PCP2, which explains the significantly larger 3P tensor elements of the PCP3 system. The large magnitude of all the components of  $\Delta\mu^{\text{ff}}$  and  $\mu^{\text{of}}$  is due to the orientation of the donor-acceptor groups in PCP3. However, on moving from the gas phase to the solvent phases, a noticeable decrease in the value of the y component of  $\mu^{\text{of}}$  in PCP3 is observed, causing a significant decrease in a large number of the 3P tensor elements which, in turn, is responsible for the overall reduction in the  $\delta^{3\text{PA}}$  values of PCP3 in THF and MeCN as compared to that of the gas phase. The solvent-dependent quenching of the charge-transfer strength in the y direction of the PCP3 molecule is evident from the differential electron density plot in Fig. 4, which explains the origin of this anomalous solvatochromic 3PA activity of PCP3.

#### 4 CONCLUSION

In conclusion, using TDDFT/CR theory and a two-state model, we have studied the effect of donor-acceptor orientation on the solvent-dependent 3PA of an unexplored class of compounds, i.e. TSCT type of molecules, namely the doubly positively charged [2, 2]-paracyclophane derivatives. The results show that the gas-phase 3P transition probabilities are as high as  $10^7$  a.u. for a particular orientation of the donor-acceptor groups and for this orientation it decreases dramatically on going from gas to solvent phase. This orientation cum solvent effect has been analyzed by inspecting the magnitude of the dominant 3P tensor components. In the gas phase, for this specific orientation of the donor-acceptor groups, the difference in the dipole moment between the ground and excited states becomes very large, thereby allowing most of the tensor elements to contribute to the overall  $\delta^{3\text{PA}}$ , making the “X” orientation the most favorable in terms of boosting the 3PA. However, in the solvent phases, the value of the ground- to excited-state transition moment decreases significantly for this particular orientation, resulting in a reduction in the corresponding  $\delta^{3\text{PA}}$  values. The differential electron density plot clearly suggests that the lowering of the charge-transfer strength in the y direction in presence of the solvent can probably be attributed to this orientation cum solvent-dependent 3PA activity for the PCP3 molecule. Although, this study is restricted to [2,2]-paracyclophane-type of molecules, in the future

other classes of compounds, including other TSCT systems, may be explored in order to investigate the transferability of this orientational dependency of the 3P activity.

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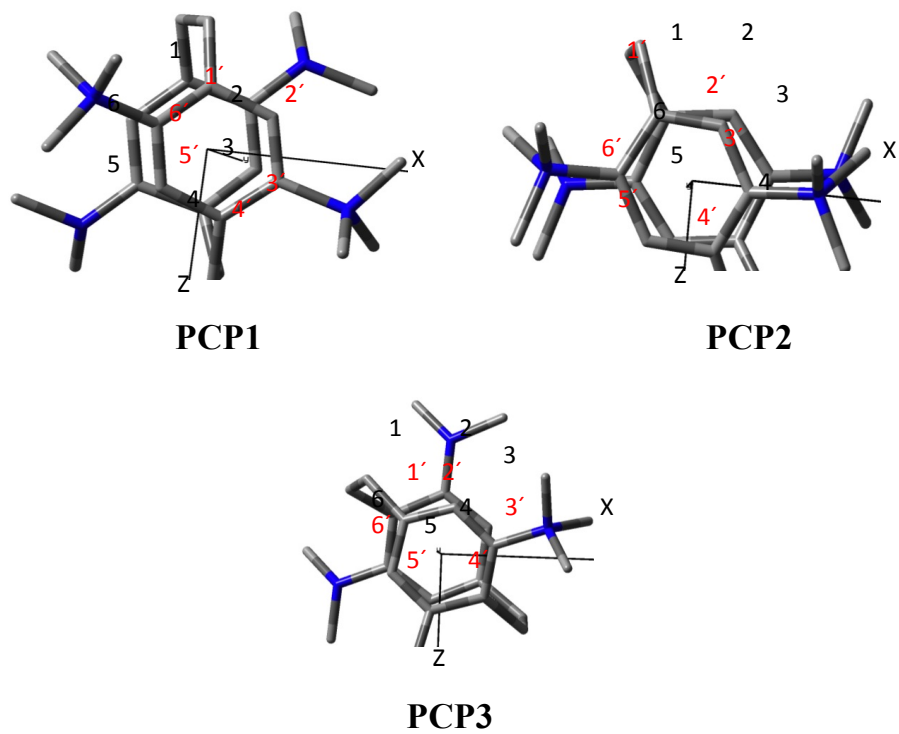
## Figure Captions

**Fig. 1** A schematic representation of the three derivatives of the doubly positively charged [2,2]-paracyclophane (PCP). The red-colored atom-labeling is for the C-atoms of the above-plane benzene ring which contains the acceptor  $-\text{NMe}_3^+$  moieties and the black ones for the below the plane benzene ring containing the donors  $-\text{NMe}_2$ .

**Fig. 2** HOMO, LUMO and differential electron density mapping (HOMO-LUMO) of PCP1 (a, b, c)

**Fig. 3** HOMO, LUMO and differential electron density mapping (HOMO-LUMO) of PCP2 (a, b, c)

**Fig. 4** HOMO, LUMO and differential electron density mapping (HOMO-LUMO) of PCP3 (g, h, i)



**Fig. 1**

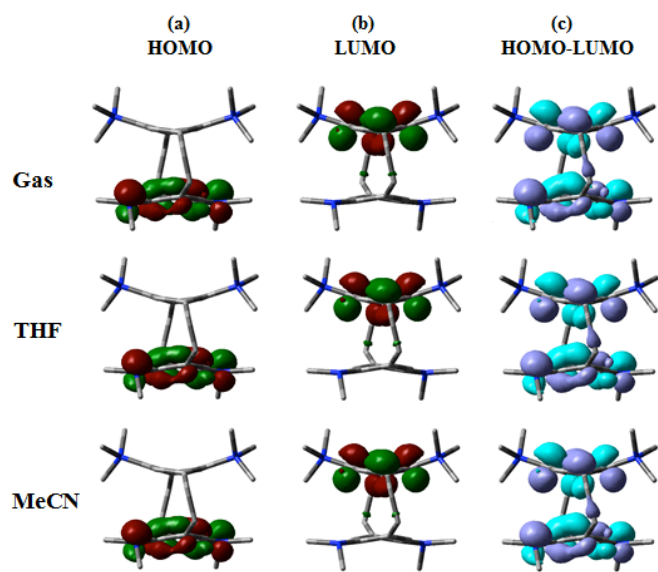


Fig. 2

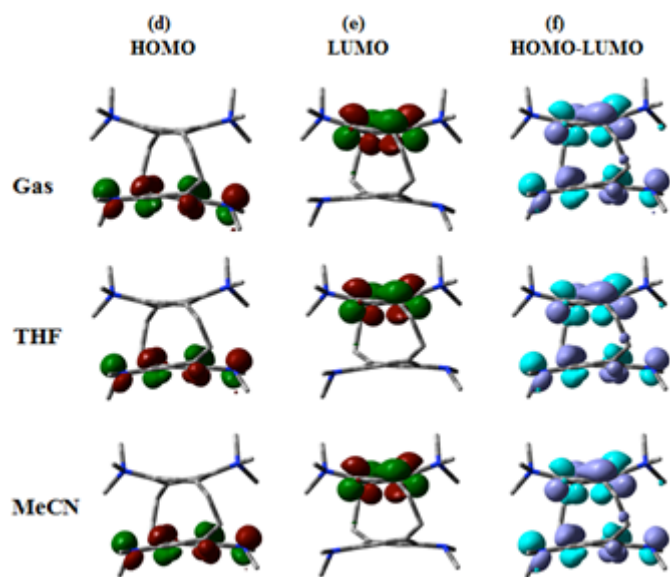
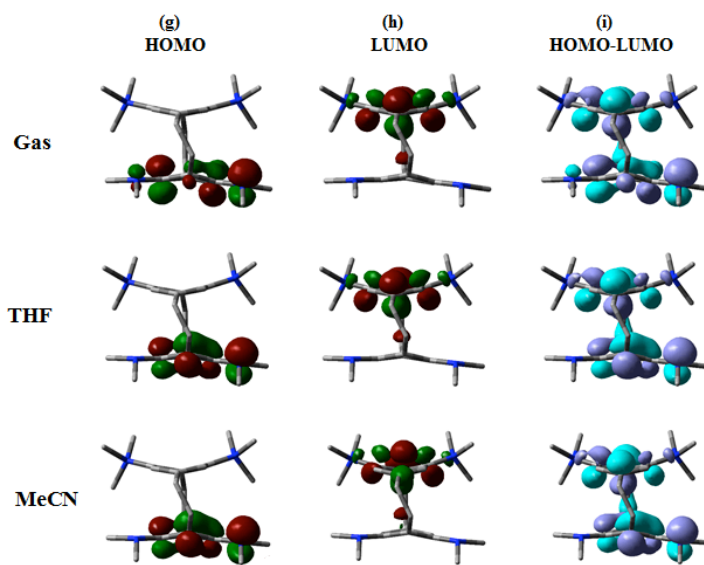


Fig. 3





**Fig. 4**

**Table 1.**  $\Delta\mu^{ff}$ ,  $\mu^{of}$ ,  $\omega_f$ ,  $\Lambda$ -parameter,  $\delta_{OPA}$  and orbitals involved in  $S_0$ - $S_1$  transition of PCP1, PCP2 and PCP3

molecules in gas and different solvent phases, calculated at CAMB3LYP/cc-pVDZ level of theory.

System	Solvent	Components of $\Delta\mu^{df}$ (a.u.)				Components of $\mu^{df}$ (a.u.)				$\omega_i$ (eV)	$\Lambda$	$\delta_{OPA}$ (a.u.)	Orbitals
		x	y	z	Total	x	y	z	Total				
PCP1	Gas	0.0	3.991	-0.0	3.991	0.136	0.0	-0.137	0.193	2.511	0.204	0.002	H-L (0.70)
	THF	0.001	4.342	-0.002	4.342	0.155	0.0	-0.155	0.219	2.951	0.216	0.002	H-L(0.70)
	MeCN	-0.002	4.296	0.001	4.296	0.159	0.0	-0.156	0.223	3.039	0.220	0.003	H-L (-0.70)
PCP2	Gas	-0.353	3.976	0.001	3.992	0.010	0.046	-0.033	0.057	2.761	0.222	0.0	H-L (-0.70)
	THF	-0.349	4.277	-0.007	4.291	0.114	0.031	-0.036	0.124	3.084	0.234	0.0	H-L(0.70)
	MeCN	-0.325	4.238	-0.005	4.250	0.112	0.034	-0.034	0.122	3.163	0.237	0.0	H-L (-0.70)
PCP3	Gas	0.913	3.674	1.408	4.039	-0.072	-0.243	-0.057	0.260	2.738	0.172	0.004	H-L (-0.66)
	THF	1.345	4.447	0.110	4.647	0.043	-0.050	-0.024	0.071	3.262	0.200	0.0	H-L(-0.69)
	MeCN	4.207	0.643	-1.615	4.552	-0.012	0.046	-0.032	0.058	3.352	0.204	0.0	H-L (-0.69)

**Table 2.**  $\delta^{3PA}$  (in  $10^6$  a.u.) and 3P tensor elements ( $T_{ijk}$ ) of the first excited state of PCP1, PCP2 and PCP3

molecules in gas and different solvents, calculated using response theory as well as 2SM at the CAMB3LYP/cc-pVDZ level of theory. The first number in last row represents the response theory results, whereas the second one is from two-state model calculations.

System	PCP1			PCP2			PCP3		
Solvent	Gas	THF	MeCN	Gas	THF	MeCN	Gas	THF	MeCN
T <sub>xxx</sub>	249.66	248.0	230.20	-582.25	535.80	495.26	-42.49	-139.11	562.93
T <sub>yyy</sub>	-29.53	-45.66	-43.79	-2140.42	1350.81	1355.02	-7651.19	-1223.07	-266.04
T <sub>zzz</sub>	-352.22	-461.86	-441.18	-28.60	-102.36	-96.42	-1203.78	-48.82	-82.75
T <sub>xyy</sub>	-0.06	0.01	1.87	119.23	-146.12	-115.29	-129.07	-141.56	-24.78
T <sub>xxz</sub>	-234.25	-259.95	-247.36	69.64	-84.11	-76.18	-33.58	47.66	-72.42
T <sub>yyx</sub>	2358.76	1979.14	1801.20	-1867.03	1881.99	1703.36	-1313.69	-447.25	-115.70
T <sub>yyz</sub>	-2379.52	-2079.93	-1904.57	659.98	-737.07	-683.65	-3310.65	-182.78	88.91
T <sub>zxx</sub>	217.47	244.10	235.42	18.92	-47.06	-46.84	-302.56	-40.95	-77.88
T <sub>zzy</sub>	-5.22	-7.16	-8.42	7.85	-36.20	-36.70	-1852.35	-36.76	-77.59
T <sub>xyz</sub>	0.01	-0.63	1.29	-0.06	2.46	3.40	-529.38	-95.83	60.69
$\delta^{3PA}$ in $10^7$ a.u.	3.39 2.71	2.65 2.56	2.23 2.25	1.85 0.93	1.50 0.74	1.28 0.65	16.30 17.91	0.34 0.48	0.05 0.14

## Notes and references

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**Electronic Supplementary Information (ESI) available:** The optimized Cartesian coordinates of all the systems in both the gas phase and in different solvents.

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