



Dye-sensitized solar cells and complexes between pyridines and iodines. A NMR, IR and DFT study

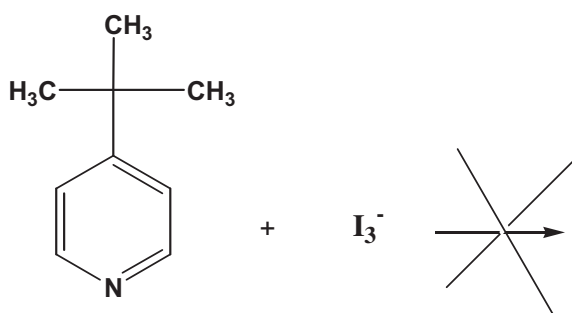
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HIGHLIGHTS

- ▶ Triiodide and pyridines are important electrolyte components in DSCs.
- ▶ Complex formation between these species has been previously suggested.
- ▶ Observed NMR shifts indicate that no such interaction takes place in CH₃CN solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Interactions between triiodide (I₃⁻) and 4-*tert*-butylpyridine (4TBP) as postulated in dye-sensitized solar cells (DSC) are investigated by means of ¹³C NMR and IR spectroscopy supported by DFT calculations. The charge transfer (CT) complex 4TBP·I₂ and potential salts such as (4TBP)₂I⁺, I₃⁻ and 4TBP at concentrations comparable to those of the DSC solar cell did not lead to any reaction. Neither CT complexes nor cationic species like (4TBP)₂I⁺ were observed, judging from the ¹³C NMR spectroscopic evidence. This questions the previously proposed formation of (4TBP)₂I⁺ in DSC cells.

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Introduction

Dye-sensitized solar cells (DSC) have been extensively studied in the last decade as a promising renewable energy source because of their potential inexpensive manufacturing technology compared to silicon cells [1–5]. In a typical DSC the electrolyte is comprised of an I⁻/I₃⁻ redox couple (0.5 M/0.05 M) in combination with a nitrogen containing additive (0.5 M), e.g., 4-*tert*-butylpyridine (4TBP) or 1-methylbenzimidazole dissolved in, e.g., 3-methoxypropionitrile [6]. The nitrogen additive increases the open circuit voltage V_{oc} of the DSC by shifting the conduction band of the

TiO₂ to more negative potentials [4,7–9]. The nitrogen additives have also been proposed to decrease the dark current of the DSC by the formation of complexes between I₃⁻ and, e.g., 4TBP as shown in Eqs. (1) and (2) [8,10,11]



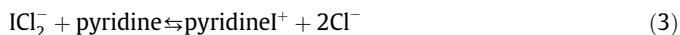
The complexes and ions formed according to Eqs. (1) and (2) are suggested to diffuse slower towards the TiO₂ photoanode than I₃⁻ itself with the result that the back electron transfer from the TiO₂ conduction band to I₃⁻ is reduced and V_{oc} increased [8,11]. Formation of the bis(4-*tert*-butylpyridine)iodonium cation, (4TBP)₂I⁺, according to Eq. (2) has also been proposed by Lund and co-workers

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[12] to reduce the thiocyanate ligand exchange rate in the N719 ruthenium dye by 4TBP at elevated temperatures.

The reason for suggesting Eq. (2) is most likely the paper by Jones et al. [13], which in turn was inspired by the work of Reid and Mulliken [14], as formulated in Eq. (3):



Jones et al. [13] reported an equilibrium constant for this reaction equal to $4.4 \times 10^4 \text{ L mol}^{-1}$ in 6 M HCl, determined by using the Benesi–Hildebrand approach. However, such acidic conditions have little relevance for the solar cell. In fact, it is difficult to see how Eq. (3) could be relevant under such conditions.

Other experimental evidence for the reaction between I_3^- and 4TBP and other pyridines is limited and only based on UV–Vis measurements of dilute solutions of 4TBP and I_3^- [11]. In contrast, the complex formation between I_2 and heteroaromatic compounds such as a variety of pyridines (Pyr) is well established [14–18]. In non-polar solvents, the charge transfer (CT) complexes (Pyr I_2) are formed exclusively [14,17] whereas in polar solvents the CT complex is formed with various amounts of ionic products such as PyrI^+ or Pyr_2I^+ [17].

The parent $(\text{pyridine})_2\text{I}^+$ salt has been characterized by X-ray crystallography [19]. Cationic species such as pyridineI^+ or $(\text{pyridine})_2\text{I}^+$ were formed in stretched polyethylene by addition of excess iodine to pyridine and characterized by IR polarization spectroscopy [20]. CT complexes and ionic product formation between alkyl substituted pyridines and iodine has been investigated by NMR using solvent mixtures of CDCl_3 and nitrobenzene [15]. The chemical shift changes induced by the formation of iodonium salts were distinctly different from those found for the simple CT complex. For DSCs, however, it is the reaction between I_3^- and nitrogen additives which is of interest. As the equilibrium constant for the reaction $\text{I}^- + \text{I}_2 \rightleftharpoons \text{I}_3^-$ in acetonitrile and similar solvents is very high, $K \approx 10^7 \text{ M}^{-1}$ [21], the distinction between I_2 and I_3^- is essential.

In view of the large interest in establishing the interactions between the components in the DSC solar cells we wish to provide tools for investigation of the interactions between I_2 or I_3^- and DSC nitrogen additives. In this context, we want to characterize the 4-*tert*-butylpyridine (4TBP) reaction products with iodine and triiodide using solid and liquid state NMR and IR spectroscopy. In particular, we want to test the proposal of Lindquist and Kusama that I_3^- may react with 4TBP according to Eqs. (1) and (2). As reference materials, the species $(4\text{TBP})_2\text{I}^+$, BF_4^- (1), $(4\text{TBP})_2\text{I}^+$, I_3^- (3) and $4\text{TBP} \cdot \text{I}_2$ (4) have been synthesized (see Fig. 1). To tie back to previous results, $(\text{pyridine})_2\text{I}^+$, BF_4^- (2) was also synthesized and investigated. The experimental results are supported by DFT calculations of ^{13}C nuclear shieldings and vibrational transitions. Additional

information is provided as [Supplementary data](#), referred to in the ensuing text as S1–S9.

Experimental

Synthesis

Bis(4-tert-butylpyridine)iodonium and bis(pyridine)iodonium tetrafluoroborate

$(4\text{TBP})_2\text{I}^+$, BF_4^- (1) and $(\text{pyridine})_2\text{I}^+$, BF_4^- (2) were synthesized by a modified literature method [22]. AgBF_4 (1.946 g, 100 mmol), 2 g TLC silica gel and CH_2Cl_2 (60 ml) was added to a 100 ml round bottom flask. 4-*tert*-Butylpyridine or pyridine (20 mmol) was added at room temperature under magnetic stirring followed by addition of I_2 (10 mmol). After 2 h at room temperature the silica gel was removed by filtration and washed by $2 \times 10 \text{ ml CH}_2\text{Cl}_2$. The combined dichloromethane was removed by rotary evaporation and the orange product was washed with cold diethyl ether and isolated by vacuum filtration. Yield of light yellow prisms 2.85 g (59%). Recrystallisation from dichloromethane/diethyl ether gave white prisms with a melting point between 131–168 °C. Elemental analysis for 1: Predicted based on $\text{C}_{18}\text{H}_{26}\text{N}_2\text{IBF}_4$: 44.66% C, 5.41% H, 5.79% N. Found: 44.24% C, 5.33% H, 5.69% N. m.p. 174 °C (starts to decompose) ^1H NMR data see S8; for ^{13}C NMR see Table 1.

Bis(4-tert-butylpyridine)iodonium triiodide

$(4\text{TBP})_2\text{I}^+$, I_3^- (3) was synthesized as described by Hassel and Hope [19]. 4-*tert*-Butylpyridine (5 mmol) in methanol (25 ml) was mixed with I_2 (5 mmol) dissolved in methanol (25 ml). Precipitation of a red compound was observed immediately. The solvent was decanted and the remaining solvent was removed by vacuum evaporation. Yield 83%.

4-tert-Butylpyridine diiodine CT complex

- (A) $4\text{TBP} \cdot \text{I}_2$ (4) was synthesized by stirring a mixture of iodine (15.7 mmol) and 4-*tert*-butylpyridine (15.7 mmol) in 230 ml hexane and 150 ml dichloromethane, leaving the mixture overnight. Orange crystals precipitated after slow evaporation of the solvent at room temperature. Elemental analysis for 4: Predicted based on $\text{C}_9\text{H}_{13}\text{N}_2$ 27.78% C, 3.34% H and 3.60% N. Found 27.84% C, 3.07% H and 3.61% N.
- (B) $4\text{TBP} \cdot \text{I}_2$ (4) 4-*tert*-butylpyridine (10 mmol) was dissolved in ethanol (140 ml) in a round bottom flask. Iodine (10 mmol) was dissolved in ethanol (10 ml) and slowly added drop wise under magnetic stirring at room temperature. The yellow precipitate was isolated by vacuum filtration and dried in a vacuum oven at 40 °C. Yield 0.98 g (25%). The product began to decompose at 96 °C.

NMR spectroscopy

The liquid state NMR spectra were recorded on a Varian Mercury 300 at 300 MHz for ^1H and 75 MHz for ^{13}C NMR using the methyl signal of acetonitrile as reference. The solid state spectra were recorded on a Varian Inova Sparc 400 instrument. Spectra were recorded with spinning speeds of both 6000 Hz and 12000 Hz.

IR spectroscopy

IR absorbance spectra were recorded at room temperature on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer in the 4000–370 cm^{-1} range with a resolution of 1 cm^{-1} (average of 10 scans). Crystalline samples of 1, 2, 3, and 4 were measured in

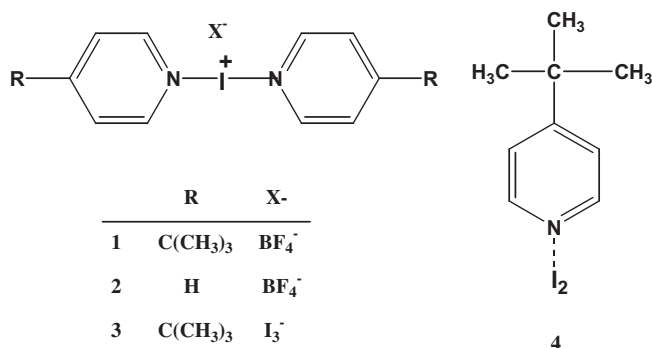


Fig. 1. Structures of compounds.

Table 1¹³C chemical shifts and complexation shifts for complexes between I₂ and pyridine or 4TBP in the liquid and the solid state.

Carbon	2 (CD ₃ CN)	2 (solid)	4TBP (CD ₃ CN)	1 (CD ₃ CN)	1 (solid)	3 (CD ₃ CN)	3 (Solid)	4 (CD ₃ CN) A ^a	4 (Solid) B ^a	4 (Solid) A ^a
C-2	150.9 (1.3) ^b	150.8	150.7	150.2 (−0.5)	149.6 [150.7] ^d	147.9 ^c (−2.8) [150.2] ^d (−0.5)	150.9 [146] ^d	148.85 ^c (−1.8) [150.15] ^d (−0.5)	147.6	148.3
C-3	129.1 (5.1)	128.2	121.8	126.0 (4.2)	126.4	123.9 ^c (2.1) [126.0] ^d (4.2)	127.5	123.3 ^c (1.5) [126.1] ^d (4.3)	126.7	127.2
C-4	143.6 (7.4)	143.2	160.9	168.4 (7.5)	168.8 ^g	165.4 (4.5) [n.o.] ^d	168.0 [165.7] ^d	163.9 ^c (3.0) [168.4] ^d (7.5)	165.7	165.7
C	–		35.3	36.6 (1.3)	37.1 ^e [36.0] ^f	36.1 (0.8) [n.o.] ^d	37.0	35.9 (0.6)	36.4	36.4
CH ₃	–		30.8	30.3 (−0.5)	31.2 ^e [30.4] ^f	30.5 (−0.3) [30.3] ^d (−0.5)	32.0	30.6 (−0.2) [30.3] (−0.5)	32.1	32.2

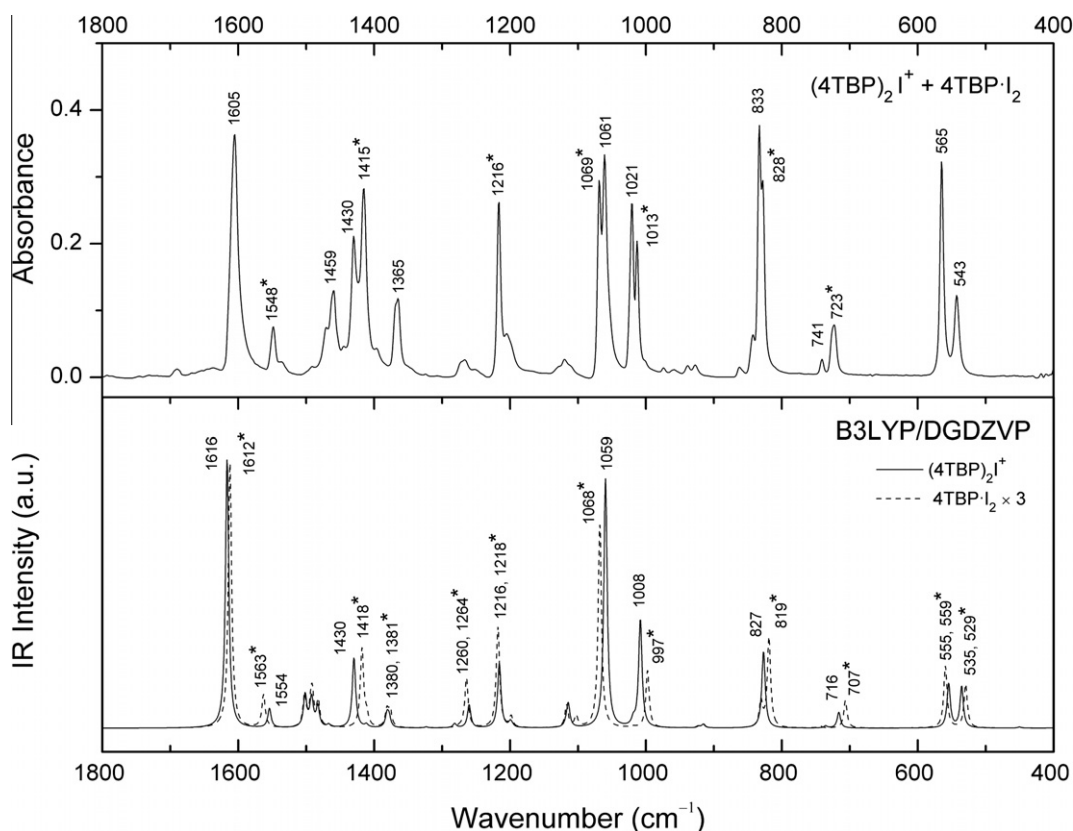
^a 4 is synthesized by methods A or B (see Experimental).^b Values in brackets are the difference in chemical shift between the complex and the non-complexed heterocycle. Values used for pyridine are: C-2 (149.6 ppm), C-3 (124.2 ppm) and C-4 (136.2 ppm).^c Major set of resonances.^d Value in bracket the less intense set of resonances. For integration see Table S8.^e The more intense resonance.^f The less intense resonance. The ratio 2:1.^g The resonance showed a multiplet splitting possibly due to through space couplings to ¹⁹F.

Fig. 2. Top: Observed IR absorbance spectrum of the red solid formed by the reaction between 4-*tert*-butylpyridine (4TBP) and diiodine in methanol solution (Sections 4-*tert*-butylpyridine diiodine CT complex and bis(4-*tert*-butylpyridine)iodonium triiodide). Bottom: Graphical representation of vibrational transitions predicted for the bis(4-*tert*-butylpyridine)iodonium cation (full line) and the 4-*tert*-butylpyridine/diiodine CT complex (4) (dashed line). The computed wavenumbers are scaled by the factor $\alpha = 0.975$ [19] and a Lorentz line shape with HWHM = 3 cm^{−1} is assumed. The relative IR intensities predicted for 4 are multiplied by a factor of 3, and peak wavenumbers for 4 are indicated by asterisks (*).

KBr tablet using standard procedures. The recorded spectra are provided as [Supplementary data S1–S4](#). The spectrum shown in [Fig. 2](#)(top) can be assigned to a mixture of 3 and 4; a full version of this spectrum is provided as [S3](#). In addition, the IR spectrum of 4TBP was recorded in CHCl₃ solution ([S5](#)).

Calculations

All calculations were performed with the Gaussian09 software package [23] by using the B3LYP density functional [24,25] with the DGDZVP all electrons basis set [26,27] as previously discussed [20].

Table 2
¹³C titration data for 4TBP and I₂ in CD₃CN.

Carbon	4TBP	4TBP: I ₂ (10:1)	4TBP: I ₂ (2:1)	4TBP: I ₂ (1:1)
C-2	150.7	150.3 (−0.4) ^a	148.9 (−1.8)	148.7 ^b (−2.0) [150.1] ^c (−0.6)
C-3	121.8	122.0 (0.2)	122.9 (1.1)	123.5 (1.7) [126.0] (4.2)
C-4	160.9	161.4 (0.6)	163.7 (2.8)	164.2 ^b
C	35.3	35.4 (0.1)	35.8 (0.5)	35.9 (0.6) [35.9] ^d (0.6)
CH ₃	30.8	30.7 (−0.1)	30.6 (−0.2)	30.5 (−0.3) [30.3] (−0.5)

^a Values in brackets are titration shifts.^b Resonance is split into two.^c Values in square brackets are due to a minor species.^d Assumed overlapping with major resonance.

In one series of calculations, molecular equilibrium geometries and vibrational transitions (harmonic approximation) were computed in the gas phase. The predicted fundamental vibrational transitions for (4TBP)₂I⁺ and 4TBP·I₂ (4) are visualized in Fig. 2(bottom).

In a second series, corresponding calculations were performed within the polarized continuum model (PCM) [28] in order to simulate the influence of an acetonitrile solvent (Gaussian09: scrf = (solvent = acetonitrile)) [23]. These calculations were carried out primarily to investigate the applicability of the free energies of reaction, ΔG, derived from the results of the harmonic analyses in Gaussian09 (298.15 K, 1 atm) [23]. Predicted ΔG values and equilibrium constants *K* for several reactions relating to the 4TBP–iodine system in acetonitrile solution are provided as Supplementary data (S6).

Judging from comparison with experimental estimates, the predicted equilibrium constants *K* seem to be reliable within one or two orders of magnitude. For example, the computed *K* for the equilibrium I₃[−] ⇌ I₂ + I[−] in acetonitrile solution is of the order 10^{−5} (S6), compared with experimental estimates in the range 10^{−6}–10^{−7} [29,30]. Similarly, the predicted *K* for the equilibrium 4TBP + I₂ ⇌ 4TBP·I₂ is close to 10¹ (S6), compared with empirical values in the range 10²–10³ [7,31]. Hence, the reaction data computed at the present, modest level of sophistication may be useful in a qualitative manner. The computed *K* values for the reactions indicated in Eqs. (1) and (2) are close to 10^{−4} and 10^{−11}, respectively (S6).

NMR nuclear shieldings were calculated in the gas phase in the GIAO approximation [31].

Results and discussion

Structures

The elemental analysis of 1 and 2 clearly showed a ratio of two pyridines to each iodine. The ¹³C NMR spectra of 1 in both CD₃CN and DMF-*d*₇ showed very clear cut spectra showing that complex formation leads to shifts in CD₃CN of 7.5 ppm (C-4), −0.5 ppm (C-2) and 4.2 ppm (C-3) relative to 4-*tert*-butylpyridine. Very similar numbers are found for the pyridine complex, 2 (see Table 1). The shifts for 1 in solution can be compared with those observed by solid state NMR and from Table 1 it is seen that very good agreement is found.

Schuster and Roberts found for the iodonium salts of pyridine and its 2,6- and 2,4,6-trimethyl derivatives the following changes of the ¹³C-shifts in nitromethane relative to the starting pyridines: C-2 (0.6, 2.9 and 2.2 ppm), C-4 (6.8, 6.6 and 9.2 ppm) and C-3 (5.1, 5.3 and 5.0 ppm). These values are comparable to those observed for salts 1 and 2. The iodonium ion (4TBP)₂I⁺ may therefore be identified by the large C-4 shift at 168 ppm.

The elemental analysis of 3 showed a ratio close to one pyridine for two iodine molecules. The solid state ¹³C spectrum of the red powder had a sharp peak at 168 ppm with a small shoulder at 164 ppm. The shift at 168 ppm shows the presence of the

iodonium ion (4TBP)₂I⁺ and the main component is therefore identified as 3. The shoulder at 164 ppm is identified as the C-4 peak in the charge transfer complex 4 (see below). Two sets of ¹³C resonances of 3 and 4 were also observed in ¹³C NMR in CD₃CN (see Table 1) and DMF-*d*₇ (see Table S7) with the 168 ppm peak (3) much smaller than the 164 peak (4). The ratio ~95:5 between 3 and 4 was obtained from the ¹H NMR spectrum in CD₃CN shown in S8. Finally, the IR spectrum of the red powder in the solid state shows two sets of characteristic bands which can be assigned to overlapping contributions from 3 and 4, in excellent consistency with the predicted vibrational transitions (Fig. 2).

The charge transfer complex 4 may be synthesized either by protocol A or B (see 4-*tert*-butylpyridine diiodine CT complex section). In synthesis A, reaction between pyridine and iodine was performed in ethanol instead of methanol and I₂ was slowly added drop wise to the 4TBP solution with formation of an orange–yellow precipitate. Both this product and the orange crystals isolated from the synthesis B reaction in hexane/CH₂Cl₂ showed a sharp peak in solid state ¹³C NMR at 165 ppm. The IR of both products showed two characteristic bands close to 1012 and 1068 cm^{−1} (S4). Elemental analysis of the orange crystals showed a 1:1 ratio between 4TBP and I₂. Based on this evidence, both products were identified as 4.

Nuclear shieldings

¹³C NMR nuclear shieldings are calculated using DFT calculations (see Experimental). The following species are calculated: 4TBP, 4, (4TBP)₂I⁺, and 4TBP⁺ (see Table 3). The experimental ¹³C shifts of 1 and 3 are nearly identical and the shifts of the (4TBP)₂I⁺ ion are therefore essentially independent of whether BF₄[−] or I₃[−] is the counter ion. It is obvious that the calculated trends are slightly different for 4TBP·I₂ and (4TBP)₂I⁺ as compared to 4TBP⁺. The data for the former have the correct signs as compared to the experimental results (Table 1), but the values are overestimated for (4TBP)₂I⁺.

Titration with I₂ and I₃[−]

Titration of 4TBP with I₂ in CD₃CN leads to complexation shifts as seen in Table 2 due to the formation of the CT complex 4 by Eq.

Table 3
Calculated ¹³C nuclear shielding σ in ppm.^a

Carbon	4TBP	4TBP·I ₂	(4TBP) ₂ I ⁺	4TBP ⁺
C-2	24.9	28.5 (3.6) ^b	29.0 (4.1)	21.3 (−3.6)
C-3	57.2	54.9 (−2.3)	51.1 (−6.1)	46.0 (−11.2)
C-4	17.7	12.9 (−4.8)	2.2 (−15.5)	−6.9 (−24.6)
C	145.0	144.5 (−0.5)	143.1 (−1.9)	140.8 (−4.2)
CH ₃	148.6	148.9 (0.3)	149.5 (0.9)	149.4 (0.8)

^a The nucleus shielding can be converted to chemical shifts with the equation δ = −0.9735σ + 176.38 (*n* = 15 *r*² = 0.9957).^b Values in brackets are complexation shifts calculated as the difference between the complex and 4TBP. Notice the different signs as compared to Table 1 because in this table we are operating with nuclear shielding.

(3). The NMR spectra were recorded in CD₃CN in order to mimic the 3-methoxypropionitrile of the solar cell, and low concentrations of 4TBP (0.30 M) are used in order to eliminate the influence of ring current effects. For the ratios I₂:4TBP of 0.1 and 0.5 only one set of resonances are seen, indicating that the forward and reverse reactions of Eq. (3) are fast compared with the NMR time scale, with the result that only the weighted ¹³C-shifts of 4TBP and 4 are observed. When an equivalent amount of I₂ is added to 4TBP in CD₃CN, a major and a minor set of ¹³C resonances are seen (Table 2). The ¹³C chemical shifts of the minor component is identical to the ¹³C shifts of 3 in CD₃CN. When the I₂: 4TBP ratio is increased from 0 to 1 the C-4 shift changes from 160 to 165 ppm which is very close to the C-4 shift 165 ppm of the orange charge transfer product 4 in CD₃CN (Table 2). The 165 ppm shift of the 1:1 titration is therefore likely to be close to the end titration value indicating that more than 90% of the 4TBP is converted to the CT complex 4. A mole fraction of 4 > 0.9 corresponds to a CT equilibrium constant K_3 of Eq. (3) > 400 in reasonable agreement with the $K = 400$ value found the reaction between 4-picoline and I₂ in nitrobenzene [32]. Attempts to titrate with excess I₂ were unsuccessful due to precipitation of 3.

In contrast, titrating 4TBP with (C₄H₉)₄N⁺, I₃⁻ leads to no change of the ¹³C chemical shifts in CD₃CN or in 4-methoxypropionitrile (Table 2). The presence of TiO₂ or heating the NMR samples for 24 h at 85 °C does not make any difference either.

Heterocyclic bases and triiodide

What happens when a heterocyclic base and triiodide are mixed as in the DSC solar cell? From Eq. (2) one could get the impression that I₃⁻ mixed with 4TBP can lead to formation of (4TBP)₂I⁺ cations. However, the ¹³C NMR spectra show clearly that no interaction takes place as no changes in the chemical shifts are observed at all, in sharp contrast to mixing 4TBP with I₂ (Table 2). This observation is consistent with the prediction that the reaction in Eq. (2) is strongly endothermic: $\Delta G \approx +15 \text{ kcal mol}^{-1}$, $K \approx 10^{-11}$ (S6).

Conclusion

¹³C NMR is a powerful tool in elucidating the interactions between species in the solar cell as demonstrated in the present case with 4TBP, but this could be any heterocyclic aromatic compound. It is demonstrated that the different species (4TBP)₂I⁺, I₃⁻ and 4TBP·I₂ can be identified. However, it is also shown that I₃⁻ does not interact significantly with 4TBP in acetonitrile or 4-methoxypropionitrile, not even in the presence of titanium dioxide or at elevated temperature. The investigation is supported by the results of DFT calculations, which are very useful for obtaining information on species that cannot immediately be observed (such as 4TBP⁺) and in obtaining approximate thermodynamic data. The combined experimental and theoretical results of the present investigation demonstrate the need for a revision of the previously suggested

DSC mechanisms based on the reactions indicated in Eqs. (1) and (2).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2012.08.006>.

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