Communication: Photoinduced carbon dioxide binding with surface-functionalized silicon quantum dots

Oscar A. Douglas-Gallardo, Cristián Gabriel Sánchez, and Esteban Vöhringer-Martinez

---

Articles you may be interested in

Communication: Biological applications of coupled-cluster frozen-density embedding
The Journal of Chemical Physics **148**, 141101 (2018); 10.1063/1.5026651

Communication: Adaptive boundaries in multiscale simulations
The Journal of Chemical Physics **148**, 141104 (2018); 10.1063/1.5025826

Perspective: Maximum caliber is a general variational principle for dynamical systems
The Journal of Chemical Physics **148**, 010901 (2018); 10.1063/1.5012990

Communication: The electronic entropy of charged defect formation and its impact on thermochemical redox cycles
The Journal of Chemical Physics **148**, 071101 (2018); 10.1063/1.5022176

Precision and accuracy in smFRET based structural studies—A benchmark study of the Fast-Nano-Positioning System
The Journal of Chemical Physics **148**, 123308 (2018); 10.1063/1.5006477

Efficient use of single molecule time traces to resolve kinetic rates, models and uncertainties
The Journal of Chemical Physics **148**, 123312 (2018); 10.1063/1.5006604
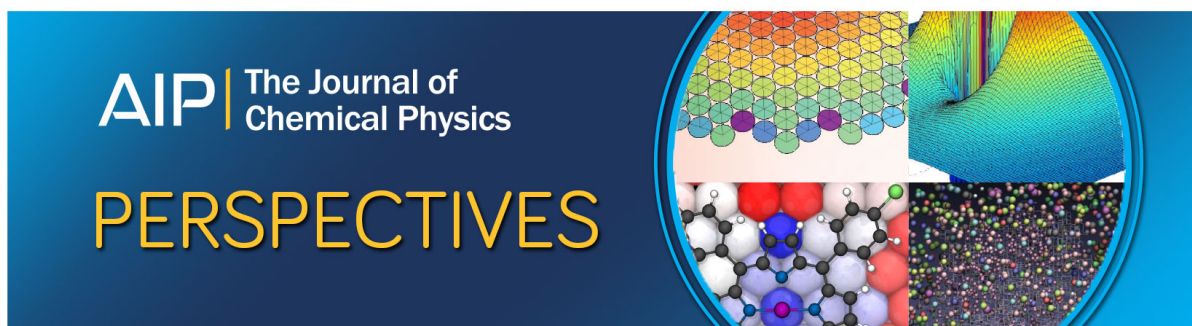
Communication: Photoinduced carbon dioxide binding with surface-functionalized silicon quantum dots

Oscar A. Douglas-Gallardo,[1] Cristián Gabriel Sánchez,[2] and Esteban Vöhringer-Martinez[1,a)]

[1]*Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile*

[2]*INFIQC (UNC-CONICET), Departamento de Química Teórica y Computacional, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina*

Nowadays, the search for efficient methods able to reduce the high atmospheric carbon dioxide concentration has turned into a very dynamic research area. Several environmental problems have been closely associated with the high atmospheric level of this greenhouse gas. Here, a novel system based on the use of surface-functionalized silicon quantum dots (*sf*-SiQDs) is theoretically proposed as a versatile device to bind carbon dioxide. Within this approach, carbon dioxide trapping is modulated by a photoinduced charge redistribution between the capping molecule and the silicon quantum dots (SiQDs). The chemical and electronic properties of the proposed SiQDs have been studied with a Density Functional Theory and Density Functional Tight-Binding (DFTB) approach along with a time-dependent model based on the DFTB framework. To the best of our knowledge, this is the first report that proposes and explores the potential application of a versatile and friendly device based on the use of *sf*-SiQDs for photochemically activated carbon dioxide fixation. *Published by AIP Publishing.* https://doi.org/10.1063/1.5027492

Carbon dioxide (CO_2) is a low molecular-weight compound that is found to be widely distributed in the atmosphere. This molecule is one of the main greenhouse gases responsible for absorbing and re-emitting solar infrared radiation over the Earth's surface.[1–3] Several environmental problems such as global warming and climate change have been associated with an increase in the atmospheric CO_2 level.[1–3] Diverse anthropogenic activities, such as industrial activity, have been pointed out as the main ecological unbalanced source leading to an increased atmospheric CO_2 concentration in the last century.[1–3] Consequently, the scouting of efficient methods for fixation, storage, capture, and harnessing of atmospheric CO_2 has become a very important research area in the last decades. Several molecular systems have been explored as efficient devices for CO_2 capture[2–15] including aliphatic amines,[6–10] semiconductor materials,[11,14,16] metallic nanostructures,[12,13] and different boron nitride nanostructures.[4,5]

In this context, Ranjan *et al.* have recently demonstrated that the modification in the oxidation state of aromatic amines can be employed as an efficient device for the reversible capture of CO_2.[17] In this approach, the fixation and release of CO_2 occur without thermal activation as in the case of the aliphatic amines.[2] The charge state of the aromatic amine (4,4′-bipyridine) defines the strength of the established chemical bond with the CO_2 molecule. When the 4,4′-bipyridine (4,4′-**Bpy**) is found in a neutral state, a very weak interaction is established [Fig. 1(a)]; but when the molecule is reduced and a net negative charge is acquired, a strong chemical bond is established [Fig. 1(b)]. In this approach, however, ionic liquids are required to establish a suitable chemical environment to stabilize the generated 4,4′-**Bpy**•⁻ radical anion reducing its transferability to aqueous systems. Furthermore, the inclusion of a suitable redox couple that is compatible with ionic liquids is needed to complete the electronic circuit, thus increasing the number of involved chemical species in the reaction scheme.

Here, an alternative system is proposed to change the charge state of the CO_2 binding aromatic amine that is based on the use of surface-functionalized silicon quantum dots (*sf*-SiQDs) to capture the CO_2 molecule through UV-visible radiation. Our proposed system rests on the underlying idea of Ranjan *et al.* that the change in the charge state on a suitable capping aromatic amine molecule is able to tune the chemical bond strength to the CO_2 molecule. Thus, in the present report, the potential use of *sf*-SiQDs as new platform is explored, which modulated by a photoinduced charge redistribution between the capping molecule and silicon quantum dots (SiQDs) is able to bind and activate the CO_2 molecule.

It is well-known that very small silicon nanostructures (diameter < 5 nm) or SiQDs exhibit interesting optoelectronic properties that depend noticeably on their size and surface state.[18–25] In general, when SiQDs are excited at their lowest electronic transition energy value, an electron-hole pair (exciton) is generated through the promotion of an electron from the valence band (VB) to the conduction band (CB). Nonetheless, a suitable surface-modification of SiQDs may open a new electronic channel through which a charge transfer process from SiQDs to the capping molecule may occur as it has been reported recently.[23,24,26] Our proposed device for CO_2

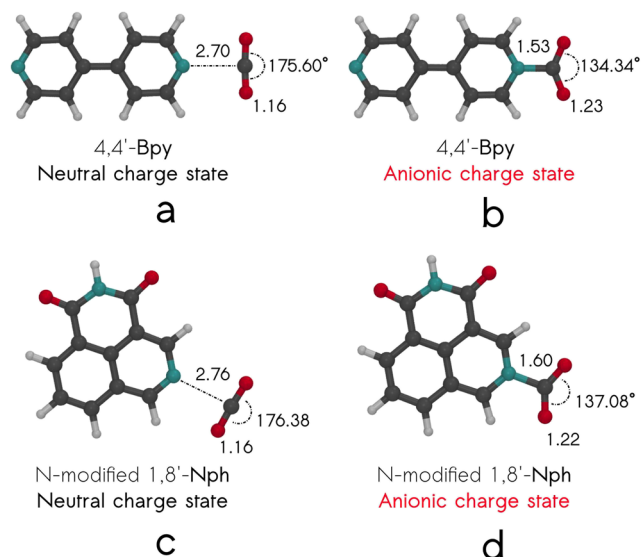a)Electronic mail: evohringer@udec.cl

FIG. 1. Calculated length and angle bonds for 4,4′-bipyridine [(a) and (b)] and N-modified 1,8-naphthalimide [(c) and (d)] in both a neutral [(a) and (c)] and anionic charge state [(b) and (d)], respectively.

activation is based on a modification in the capping molecule of *sf*-SiQDs obtained from the synthesis route recently proposed by Zhong *et al.*[27] In this synthetic approach, the *sf*-SiQDs are produced photochemically under mild-conditions with UV irradiation at room temperature using 1,8-naphthalimide (1,8-**Nph**) as both a reducing agent and surface ligand. The as-prepared *sf*-SiQDs exhibit highly tunable fluorescent properties with a large quantum yield (25%) and high photochemical stability. These SiQDs are surface-capped with 1,8-**Nph** which modifies their optical properties and increases their water solubility. An interesting feature that these *sf*-SiQDs exhibit is the localization of their Frontier Molecular Orbital (FMO): their Highest Occupied Molecular Orbital (HOMO) is delocalized over the whole SiQDs while their Lowest Unoccupied Molecular Orbital (LUMO) is delocalized over the capping molecule.[27] This special feature enables an electronic channel where a charge transfer process could take place from the SiQDs to the capping molecule driven by an optical excitation.

In this context, an alternative device for CO_2 activation is proposed here changing one carbon atom at one of the 1,8-**Nph** aromatic rings with a nitrogen atom [Figs. 1(c) and 1(d)] in order to hold a similar CO_2 binding site as is exhibited in 4,4′-**Bpy**. This modification would include the necessary atomic environment to capture CO_2 once a charge transfer process is stimulated and the aromatic amine has acquired a negative charge. In this case, and in contrast to Ranjan *et al.* report, the negative charge over aromatic amines is accomplished by a charge redistribution triggered by the optical energy absorption processes that happens on the SiQDs *in lieu* of the electrochemical reduction reaction. This has the advantage that CO_2 capture will become a triggered process by photochemical activation that is simpler than electrochemical activation, which requires the presence of a redox couple and special solvents as ionic liquids. Likewise, in principle, the lifetime of the anionic species could be tuned with the excitation source.

In order to assess the feasibility of our proposed device for CO_2 activation, the study on the molecular system has been separated into two parts. First, the electron affinity and interaction energy between the proposed capping molecule (N-modified 1,8-naphthalimide: N-modified 1,8-**Nph**) and CO_2 have been addressed and compared with the electronic and chemical properties of 4,4′-**Bpy** by Density Functional Theory (DFT) calculation with the software package ORCA.[28,29] A range-separated exchange-correlation (xc) functional (ωB97x-D3) has been employed to determine the electronic structure of these systems with the *ma*-def2-TZVPP and def2-TZVPP basis set to describe the anionic and neutral species, respectively. The second part addresses the feasibility of the electron transfer process within *sf*-SiQDs by using N-modified 1,8-**Nph** as a capping molecule. The electronic structure calculations for the electron transfer process were done with the Density Functional Tight-Binding (DFTB)[30–32] method as implemented in DFTB+[33] along with a pbc-0-3[20,34–36] DFTB parameter set. Similarly, the electronic dynamics have been simulated through a time-dependent method based on the DFTB (TD-DFTB) approach developed by Sanchez's group.[37–39] A complete description of the employed theoretical methodology can be found in the supplementary material.

As mentioned above, a net negative charge over the capping molecule (N-modified 1,8-**Nph**) or aromatic amines (4,4′-**Bpy**) is required to chemically bind CO_2. A quantitative measure of the capability of a molecule to gain an electron is defined by its electron affinity. This property can be determined through an electronic structure calculation. In Table I, the adiabatic (EA_{ad}) and vertical (EA_v) electron affinity[40] of 4,4′-**Bpy**, 1,8-**Nph**, and N-modified 1,8-**Nph** are shown. The adiabatic and vertical electron affinity is obtained from the difference of two separated electronic energy calculations by using the following definitions: $EA_{ad} = E_N^{Opt} - E_{N+1}^{Opt}$ and $EA_v = E_N^{Opt} - E_{N+1}^{sp}$, respectively. Here, N is the number of electrons in the system and the superscripts make reference to whether the electronic structure calculation has been done at the optimized geometry of the neutral species [a single point (sp)] or a complete geometry optimization (opt) calculation has been performed. If this value is positive, the anionic species is more stable than neutral species. As shown in Table I, the calculated electron affinities of all molecules are positive which is indicative that these molecules are prone to take an electron and therefore to bear negative charge. The highest value is obtained for the proposed capping molecule (N-modified 1,8-**Nph**) for all definitions of the electron affinity.

After having shown that N-modified 1,8-**Nph** is prone to be reduced, its capability to capture CO_2 in the neutral [Fig. 1(c)] and reduced state [Fig. 1(d)] can be assessed

TABLE I. Electron affinity obtained for different target molecules. The energy is expressed in eV. Calculations were done using the ωB97x-D3 functional and *ma*-def2-TZVPP basis set.

Electron affinity	4,4′-**Bpy**	1,8-**Nph**	N-modified 1,8-**Nph**
EA_{ad}	0.66	1.24	1.52
EA_v	0.45	1.08	1.35

through the calculation of the interaction energy between both molecules. The obtained results are compared with the obtained chemical properties of 4,4′-**Bpy** as a reference system in both states [Figs. 1(a) and 1(b)]. As it is shown in Fig. 1, the charge state of N-modified 1,8-**Nph** determines the strength of the established chemical bond between these aromatic amines and the CO_2 molecule. When the N-modified 1,8-**Nph** is found in a neutral state, a weak non-covalent bond is established between both molecules. The calculated interaction energy in the neutral state for N-modified 1,8-**Nph** is −4.6 kJ/mol (corrected for zero-point energy), which is very close to the obtained value for 4,4′-**Bpy** of −5.9 kJ/mol. In both neutral systems [see Figs. 1(a) and 1(c)], only small structural modifications are detected in the CO_2 molecule. The obtained structure is characterized by a subtle modification of the CO bond length (1.16 Å) and the OCO angle bond (176.38°) within the CO_2 molecule, as is schematically shown in Fig. 1(c) [or Fig. 1(a)]. The obtained distance between the carbon atom of CO_2 and the aromatic amine nitrogen atom for N-modified 1,8-**Nph** is 2.76 Å. The same structural parameters for 4,4′-**Bpy** turned out to be 1.16 Å, 175.60°, and 2.70 Å [Fig. 1(a)].

When the N-modified 1,8-**Nph** is negatively charged, a stronger interaction is established between both molecules. The calculated interaction energy for the reduced N-modified 1,8-**Nph** is −17.4 kJ/mol, which is larger than the obtained value in a neutral charge state (−4.6 kJ/mol). The obtained value for the interaction energy in 4,4′-**Bpy** was −58.1 kJ/mol. In the case of the anionic N-modified 1,8-**Nph** complex, the optimized structure exhibits a noticeable distortion of the angle (137.08°) and bond length (1.22 Å) associated with the CO_2 molecule [see Fig. 1(d)]. A shorter distance is obtained between the carbon atom of the CO_2 and the aromatic amine nitrogen atom (1.60 Å), which is in agreement with a stronger interaction, as is shown in Fig. 1(d). For 4,4′-**Bpy**, the structural parameters are comparable with values of 1.23 Å, 134.34°, and 1.53 Å. It is important to stress that the structural modification of the CO_2 molecule can be attributed to a charge transfer process from the aromatic amine to the CO_2 molecule. This charge transfer is confirmed by the sum of the calculated Mulliken atomic charges over the carbon dioxide molecule (or carboxylate groups), which is −0.442 e and −0.512 e for N-modified 1,8-**Nph** and 4,4′-**Bpy**, respectively. These values are very close to those reported in Refs. 5 and 41. These results demonstrate that a strong interaction can be established between the carbon atom of CO_2 and the nitrogen atom within N-modified 1,8-**Nph** when the aromatic amines acquire a negative charge.

One possibility to produce a partial negative charge on the N-modified 1,8-**Nph** to bind CO_2 is by means of a charge transfer process from the SiQDs to a capping molecule driven by an optical energy absorption process. The FMO associated with the N-modified 1,8-**Nph**-saturated SiQDs (mNph-SiQDs) is shown in Fig. 2 and compared with hydrogen-saturated SiQDs (H-SiQDs). We have chosen to use H-SiQDs as a reference system due to the negligible effect of the hydrogen atoms over the optical properties of SiQDs.[19] As it can be observed, in the case of H-SiQDs, the HOMO and LUMO are both delocalized on the whole SiQDs; while in the case of mNph-SiQDs, a split out in the localization of the FMO is observed. Here,
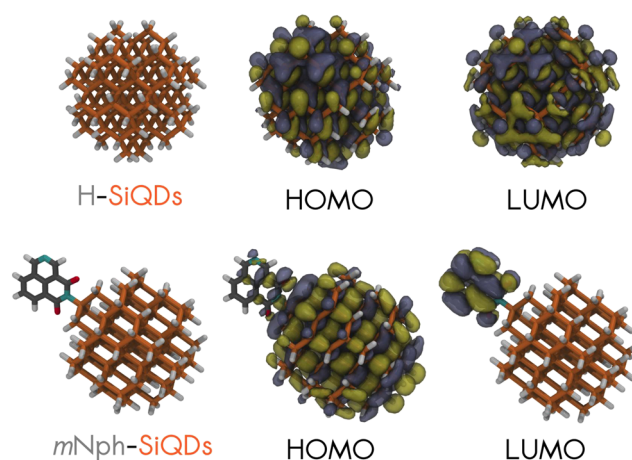

FIG. 2. Frontier molecular orbitals associated with H-SiQDs and mNph-SiQDs. An isovalue of 0.005 e/a_0^3 was used for both systems.

the HOMO is delocalized over whole SiQDs but the LUMO is located only at the capping molecule (N-modified 1,8-**Nph**), in agreement with Zhong et al.[27] The split out in FMO can also be observed through the partial density of state (pDOS) of both sf-SiQDs. The pDOS associated with H-SiQDs is shown in Fig. 3(a). The most important feature is a forbidden energy
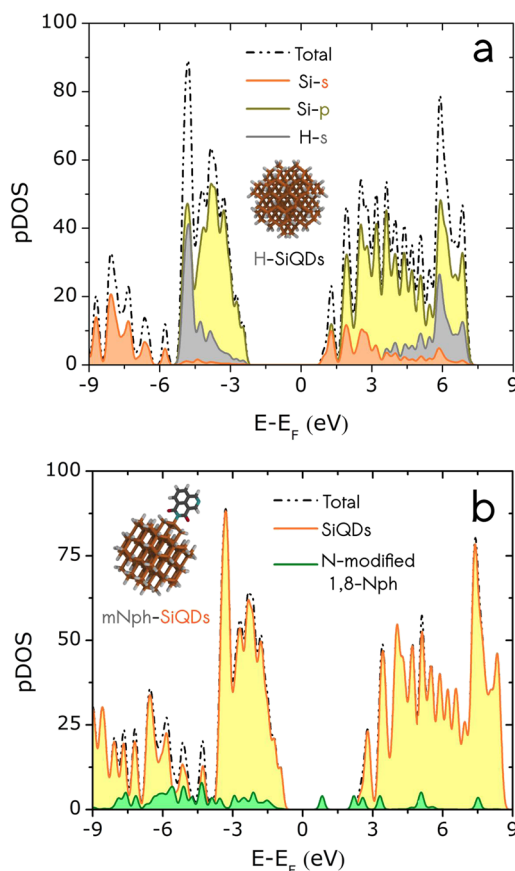

FIG. 3. (a) Partial density of state (pDOS) associated with H-SiQDs projected over all silicon orbital-shells (s-shell: orange color and p-shell: yellow color) and over the hydrogen orbital shells (s-shell: gray color). (b) Partial density of state of the mNph-SiQDs projected over the capping molecule (green color) and the silicon nanostructure (yellow color). In both cases, the total density of state is represented as a black dotted line.

zone denominated band gap between VB and CB whose separation is intimately related with its size and surface state.[18–22] The N-modified 1,8-**Nph** molecule introduces a set of molecular states within this band gap setting a new LUMO state for the whole system [Fig. 3(b), green zone]. This molecular orbital does not undergo an appreciable mixing with the molecular orbitals of the SiQDs as evidenced by comparison of the LUMO associated with whole *sf*-SiQDs and the isolated molecule (see Fig. S1 in the supplementary material).

As it has been mentioned before, the spatial separation in FMO enables the existence of an electronic channel where a charge transfer process from SiQDs to the capping molecule may occur. In order to promote this charge transfer process, the lowest electronic transition energy has to be determined. For this propose, the optical absorption spectrum of the whole system has been calculated using the TD-DFTB method. The optical absorption spectra of the isolated N-modified 1,8-**Nph** molecule, H-SiQDs and *m*Nph-SiQDs, are shown in Fig. 4. The optical absorption spectrum of *m*Nph-SiQDs is characterized by an increased absorption band within the UV-visible region. The lowest excitation energy is located at 3.45 eV and corresponds to the HOMO-LUMO transition described above revealing a red shift for the electronic excitation energy when the N-modified 1,8-**Nph** is included (red dotted and black solid line in Fig. 4).

To perform a detailed study on the charge transfer process upon irradiation, continuous excitation of *m*Nph-SiQDs was simulated using a sinusoidal time-dependent electric field as external perturbation. This allows disclosure of the underlying dynamics that characterize the excited electron motion associated with the HOMO-LUMO electronic transition. To monitor the charge transfer, the variation of the sum of the atomic Mulliken charges on the capping molecule and the SiQDs as a consequence of laser illuminations are shown in Fig. 5. As it can be observed, there exists an ultra-fast charge transfer process between the SiQDs and the capping molecule. This charge transfer process reaches a steady and stable character once it is produced with no back-transfer in the times studied. This charge transfer also happens under the physisorption of carbon dioxide to the capping molecule as shown in Fig. S2 in the supplementary material.
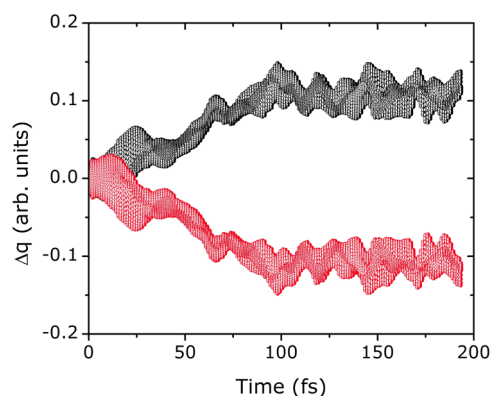
FIG. 5. Evolution of the total charge (Mulliken charges) for both parts of the system under continuous laser illumination: SiQDs (black empty circles) and the capping molecule N-modified 1,8-**Nph** (red empty circle). The excitation energy is tuned to the lowest electronic transition energy associated with the *m*Nph-SiQDs at 3.45 eV and with an electric field intensity of $E_0 = 0.05$ V/Å. The obtained charge is shown relatively to the initial charge.

Considering our previous result that a negative charge on N-modified 1,8-**Nph** increases the interaction energy and the bond strength to CO_2, one can conclude that the extra charge on the capping molecule after irradiation will induce a stronger interaction with CO_2. This binding process will be triggered by irradiation and may be reversible if no other de-excitation channels become dominant. Consequently, the molecular system may serve as a switchable device that binds CO_2 after irradiation as has been proposed.

The general operation of our device for photoinduced CO_2 activation can be summarized as follows: In the absence of UV-visible radiation (3.45 eV–358 nm) only a very weak non-covalent interaction between the capping molecule and CO_2 may be established, since the aromatic amine is found in a neutral state. When the *m*Nph-SiQDs are illuminated with a suitable frequency (~358 nm), a charge transfer process is trigged from the SiQDs to the capping molecule. During this ultrafast process, the capping molecule acquires a partial negative charge that strengthens the interaction with the CO_2 molecule. In this case, the aromatic amines' partial anionic form is produced by a photoinduced charge redistribution in the whole system *in lieu* of a chemical reduction reaction as in the 4,4′-**Bpy** case. Here, it is important to stress that the effect of just one capping molecule as a model system to activate the CO_2 molecule has been explored. However, under experimental conditions, silicon quantum dots should have an almost complete coverage of capping molecules on their surface, to which the same charge transfer process may occur.

Likewise, it is important to stress that this proposed device exhibits other attractive features. As it has been noted before, SiQDs exhibit strong fluorescent properties that depend markedly on their size and surface state. Therefore, the change from the switch-off to switch-on state could be monitored by the modifications of the optical absorption and fluorescent properties. Similarly, Fourier Transform Infrared (FT-IR) vibrational spectroscopy in a pump-probe arrangement could be also used as a suitable spectroscopic tool in order to detect and assess the carbon dioxide fixation. As shown in Fig. S3
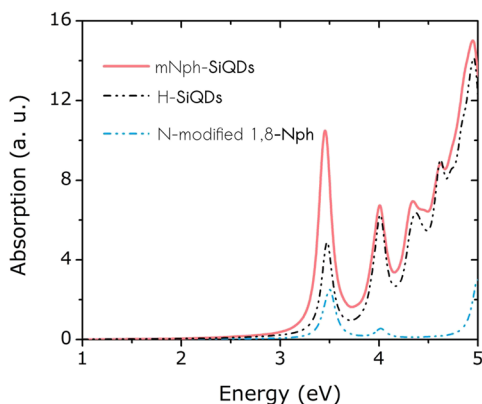
FIG. 4. Optical absorption spectra corresponding to N-modified 1,8-naphthalimide molecules (cyan dotted line), H-SiQDs (black dotted line), and *m*Nph-SiQDs (red solid line).

in the supplementary material, the asymmetric stretching frequency of the CO_2 molecule is sensitively modified with the strength of the established chemical bond between CO_2 and the capping aromatic amine molecule.

In summary, in the present report, the use of *sf*-SiQDs as an alternative device for CO_2 trapping has been theoretically explored and presented as a proof of concept. Binding of CO_2 is accomplished as a consequence of a photoinduced charge transfer process from SiQDs to the capping molecule. This split out of charge generates a partial negative charge on the molecule inducing a strengthening in the interaction with CO_2. Our results show that the use of *sf*-SiQDs could open new pathways in the development of more efficient devices for CO_2 trapping, which has to be validated experimentally. Furthermore, the employment of SiQDs with different sizes and surface moieties could even enrich the possibility to modulate CO_2 fixation.

See supplementary material for details of the computational methods, the Frontier Molecular Orbital of N-modified-1,8 naphthalimide, the evolution of the Mulliken charges for the surface modified SiQDs interacting with CO_2, and the infrared spectra of the molecular systems in Fig. 1.

[1] J. G. Vitillo, RSC Adv. **5**, 36192 (2015).

[2] M. Mikkelsen, M. Jorgensen, and F. C. Krebs, Energy Environ. Sci. **3**, 43 (2010).

[3] H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, and I. Wright, J. Environ. Sci. **20**, 14 (2008).

[4] H. Choi, Y. C. Park, Y.-H. Kim, and Y. S. Lee, J. Am. Chem. Soc. **133**, 2084 (2011).

[5] Q. Sun, Z. Li, D. J. Searles, Y. Chen, G. M. Lu, and A. Du, J. Am. Chem. Soc. **135**, 8246 (2013).

[6] G. T. Rochelle, Science **325**, 1652 (2009).

[7] F. Barzagli, F. Mani, and M. Peruzzini, Energy Environ. Sci. **2**, 322 (2009).

[8] Y. S. Jun and L. Huen, Chem. Lett. **32**, 344 (2003).

[9] J.-Y. Park, S. J. Yoon, and H. Lee, Environ. Sci. Technol. **37**, 1670 (2003).

[10] R. A. Khatri, S. S. C. Chuang, Y. Soong, and M. Gray, Energy Fuels **20**, 1514 (2006).

[11] P. Usubharatana, D. McMartin, A. Veawab, and P. Tontiwachwuthikul, Ind. Eng. Chem. Res. **45**, 2558 (2006).

[12] D. Kim, J. Resasco, Y. Yu, A. M. Asiri, and P. Yang, Nat. Commun. **5**, 4948 (2014).

[13] W. Zhu, R. Michalsky, O. Metin, H. Lv, S. Guo, C. J. Wright, X. Sun, A. A. Peterson, and S. Sun, J. Am. Chem. Soc. **135**, 16833 (2013).

[14] C. Peng, G. Reid, H. Wang, and P. Hu, J. Chem. Phys. **147**, 030901 (2017).

[15] L. J. Murphy, K. N. Robertson, R. A. Kemp, H. M. Tuononen, and J. A. C. Clyburne, Chem. Commun. **51**, 3942 (2015).

[16] W. Sun, C. Qian, L. He, K. K. Ghuman, A. P. Y. Wong, J. Jia, A. A. Jelle, P. G. O'Brien, L. M. Reyes, T. E. Wood, A. S. Helmy, C. A. Mims, C. V. Singh, and G. A. Ozin, Nat. Commun. **7**, 12553 (2016).

[17] R. Ranjan, J. Olson, P. Singh, E. D. Lorance, D. A. Buttry, and I. R. Gould, J. Phys. Chem. Lett. **6**, 4943 (2015).

[18] X. Cheng, S. B. Lowe, P. J. Reece, and J. J. Gooding, Chem. Soc. Rev. **43**, 2680 (2014).

[19] Q. S. Li, R. Q. Zhang, S. T. Lee, T. A. Niehaus, and T. Frauenheim, J. Chem. Phys. **128**, 244714 (2008).

[20] H. F. Wilson, L. McKenzie-Sell, and A. S. Barnard, J. Mater. Chem. C **2**, 9451 (2014).

[21] C. M. Hessel, D. Reid, M. G. Panthani, M. R. Rasch, B. W. Goodfellow, J. Wei, H. Fujii, V. Akhavan, and B. A. Korgel, Chem. Mater. **24**, 393 (2012).

[22] M. Dasog, G. B. De los Reyes, L. V. Titova, F. A. Hegmann, and J. G. C. Veinot, ACS Nano **8**, 9636 (2014).

[23] T. Zhou, R. T. Anderson, H. Li, J. Bell, Y. Yang, B. P. Gorman, S. Pylypenko, M. T. Lusk, and A. Sellinger, Nano Lett. **15**, 3657 (2015).

[24] Q. Li, T.-Y. Luo, M. Zhou, H. Abroshan, J. Huang, H. J. Kim, N. L. Rosi, Z. Shao, and R. Jin, ACS Nano **10**, 8385 (2016).

[25] Z. Kang, C. H. A. Tsang, N.-B. Wong, Z. Zhang, and S.-T. Lee, J. Am. Chem. Soc. **129**, 12090 (2007).

[26] G. B. De los Reyes, M. Dasog, M. Na, L. V. Titova, J. G. C. Veinot, and F. A. Hegmann, Phys. Chem. Chem. Phys. **17**, 30125 (2015).

[27] Y. Zhong, X. Sun, S. Wang, F. Peng, F. Bao, Y. Su, Y. Li, S.-T. Lee, and Y. He, ACS Nano **9**, 5958 (2015).

[28] F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **8**, e1327 (2018).

[29] F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 73 (2012).

[30] M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai, and G. Seifert, Phys. Rev. B **58**, 7260 (1998).

[31] P. Koskinen and V. Mäkinen, Comput. Mater. Sci. **47**, 237 (2009).

[32] M. Elstner and G. Seifert, Philos. Trans. R. Soc., A **372**, 20120483 (2014).

[33] B. Aradi, B. Hourahine, and T. Frauenheim, J. Phys. Chem. A **111**, 5678 (2007).

[34] E. Rauls, J. Elsner, R. Gutierrez, and T. Frauenheim, Solid State Commun. **111**, 459 (1999).

[35] C. Kohler, Z. Hajnal, P. Deak, T. Frauenheim, and S. Suhai, Phys. Rev. B **64**, 085333 (2001).

[36] A. Sieck, T. Frauenheim, and K. A. Jackson, Phys. Status Solidi B **240**, 537 (2003).

[37] O. A. Douglas-Gallardo, M. Berdakin, and C. G. Sánchez, J. Phys. Chem. C **120**, 24389 (2016).

[38] M. B. Oviedo, X. Zarate, C. F. A. Negre, E. Schott, R. Arratia-Pérez, and C. G. Sánchez, J. Phys. Chem. Lett. **3**, 2548 (2012).

[39] C. F. A. Negre, V. C. Fuertes, M. B. Oviedo, F. Y. Oliva, and C. G. Sánchez, J. Phys. Chem. C **116**, 14748 (2012).

[40] K. D. Jordan, V. K. Voora, and J. Simons, Theor. Chem. Acc. **133**, 1445 (2014).

[41] Q. Sun, G. Qin, Y. Ma, W. Wang, P. Li, A. Du, and Z. Li, Nanoscale **9**, 19 (2017).