ChemComm

RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 4474

Received 13th February 2013,
Accepted 26th March 2013

DOI: 10.1039/c3cc41187g

www.rsc.org/chemcomm

Enhanced photoelectrochemical performance of composite photovoltaic cells of Li^+@C_{60}–sulphonated porphyrin supramolecular nanoclusters†

Kei Ohkubo,[a] Yuki Kawashima,[a] Hayato Sakai,[b] Taku Hasobe*[b] and Shunichi Fukuzumi*[ac]

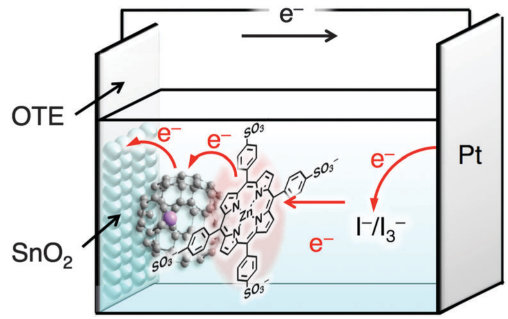
A photoelectrochemical solar cell composed of supramolecular nanoclusters of lithium encapsulated fullerene and zinc sulphonated *meso*-tetraphenylporphyrin exhibits significant enhancement in the photoelectrochemical performance as compared with the reference system containing only a single component.

Photoelectrochemical cells (PECs) have been widely investigated as a next-generation solar cell because of their simple structure.[1–3] The photoinduced charge separation between the excited state of dye and the electrode plays an important role in improvement of PEC performance. In the natural photosynthetic reaction centre, the efficient photoinduced electron transfer occurs to give a long-lived charge separated (CS) state with high quantum yield.[4] Extensive efforts have so far been devoted to design and synthesize electron donor–acceptor linked molecules to achieve efficient photoinduced charge separation for applications to PECs.[5,6] However, the synthetic difficulty of the covalently linked donor–acceptor molecule has precluded the development of simple photovoltaic devices using such model compounds of the photosynthetic reaction centre. Among many candidates, porphyrins and fullerenes are a suitable combination for the construction of PECs, because porphyrins have strong visible absorption bands and fullerene exhibits efficient electron-transfer properties such as small reorganization energy due to the delocalized three-dimensional π-system.[7] The supramolecular approaches for PECs are also investigated, however, there was no report of supramolecules with a strong binding between neutral porphyrins and fullerenes.

We have recently designed and synthesized simple electron donor–acceptor supramolecular complexes composed of lithium ion encapsulated fullerene (Li^+@C_{60}) and sulphonated *meso*-tetraphenylporphyrin ($MTPPS^{4-}$: M = Zn, H_2), which have strong 1 : 1 supramolecular binding due to the cation–anion and π–π interactions ($K = \sim 10^5\ M^{-1}$).[8] Photoexcitation of the supramolecule exhibited extremely slow charge-recombination of the CS state (τ = 0.3 ms) in benzonitrile (PhCN).[8] Li^+@C_{60} has been reported to act as a more effective electron acceptor than pristine C_{60}.[9] The driving force of photoinduced electron transfer from $MTPPS^{4-}$ to the triplet excited state of Li^+@C_{60} is highly positive ($-\Delta G_{ET}$ = 0.98 eV for $ZnTPPS^{4-}$ and 0.67 eV for H_2TPPS^{4-} in polar PhCN),[8] which is large enough to afford the CS states even under the non-polar environment in nanoclusters.

We report herein photovoltaic cells using Li^+@C_{60}–$MTPPS^{4-}$ nanoclusters, which are assembled on the optically transparent electrode (OTE) of nanostructured SnO_2 (OTE/SnO_2). The photoelectrochemical behaviour of the nanostructured SnO_2 film of supramolecular nanoclusters between Li^+@C_{60} and $MTPPS^{4-}$ denoted OTE/SnO_2–($MTPPS^{4-}$–Li^+@C_{60})$_n$ is significantly higher than the single component films of $MTPPS^{4-}$ or Li^+@C_{60} clusters, denoted OTE/SnO_2–($MTPPS^{4-}$)$_n$ or OTE/SnO_2–(Li^+@C_{60})$_n$ (Scheme 1).

A solution of Li^+@C_{60}–$MTPPS^{4-}$ supramolecule was prepared by mixing Li^+@$C_{60}PF_6^-$ (2.5×10^{-4} M) and $(Bu_4N^+)_4$ $MTPPS^{4-}$ (2.5×10^{-4} M) in PhCN. The mother PhCN solution of 1 mL was injected to an acetonitrile (MeCN) solution (3 mL) to produce the suspension containing the supramolecular



Scheme 1 Schematic image of a photoelectrochemical cell of OTE/SnO_2–$MTPPS^{4-}$–Li^+@C_{60}.

---

[a] Department of Material and Life Science, Graduate School of Engineering, Osaka University and ALCA, Japan Science and Technology Agency (JST), 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-7370; Tel: +81-6-6879-7368

[b] Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama, 223-8522, Japan. E-mail: hasobe@chem.keio.ac.jp

[c] Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea

† Electronic supplementary information (ESI) available: Spectral data and experimental details. See DOI: 10.1039/c3cc41187g

nanoclusters [$(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$]. The suspension of $(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ was transferred into a cuvette, in which the two electrodes OTE and OTE/$\mathrm{SnO_2}$ were placed and kept at a distance of 5 mm using a Teflon spacer. Then, application of the DC electric field ($\sim$100 V cm^{-1}) resulted in the deposition of $(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ from the suspension to the electrode surface and the formation of a robust thin film of OTE/$\mathrm{SnO_2}$–$(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$, as documented by discoloration of the suspension and the simultaneous coloration of the OTE/$\mathrm{SnO_2}$ electrode. For reference purposes, a thin film of only $\mathrm{Li}^{+}@\mathrm{C}_{60}$ or MTPPS was analogously deposited onto the electrode surface to form OTE/$\mathrm{SnO_2}$–$(\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ or OTE/$\mathrm{SnO_2}$–$(\mathrm{MTPPS})_n$.

Steady-state UV-vis absorption spectroscopy was used to follow the deposition of the $\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60}$ supramolecular material onto the electrode surface. The UV-vis absorption spectra of OTE/$\mathrm{SnO_2}$–$(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ are shown in Fig. 1, exhibiting significant broadening as compared with those in PhCN solutions of MTPPS^{4-}. Such broadening behaviour indicates that the molecular environment on the OTE/$\mathrm{SnO_2}$ surface is significantly perturbed because of the aggregation of the porphyrin molecules or the supramolecules by π-stacking. Thus, $\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60}$ is successfully deposited on OTE/$\mathrm{SnO_2}$. The broad absorption band at 725 nm shown in Fig. 1a may be assigned to the charge-transfer band between the porphyrin plane and the fullerene sphere in the 1 : 1 supramolecular complex as reported previously.[10]

TEM was used to evaluate the topography of an OTE/$\mathrm{SnO_2}$–$(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ film as shown in Fig. 2. The $(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ films are composed of closely packed MTPPS^{4-} and $\mathrm{Li}^{+}@\mathrm{C}_{60}$ composite clusters of about 80 nm in size, which renders a nanoporous morphology to the film. The cluster sizes were also evaluated by the dynamic light scattering (DLS) measurements (see Fig. S1 in the ESI†). The grape bunch morphology of the cluster assembly thus provides a high surface area to the electrophoretically deposited film of $\mathrm{Li}^{+}@\mathrm{C}_{60}$ clusters. As indicated earlier,[11] charging of porphyrin and fullerene moieties in the DC electric field plays an important role in the growth and deposition process. These films are quite robust and can be washed with organic solvents to remove any loosely bound MTPPS^{4-} and $\mathrm{Li}^{+}@\mathrm{C}_{60}$ nano-assemblies.

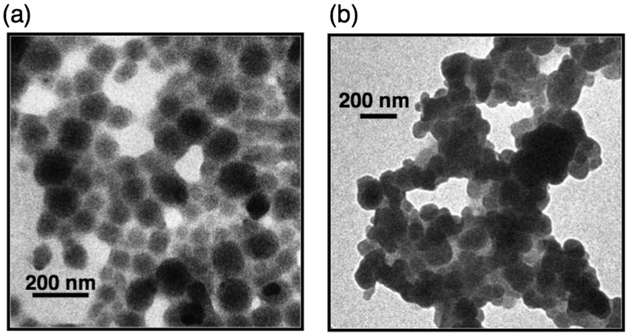


Fig. 2 TEM images of (a) $\mathrm{Li}^{+}@\mathrm{C}_{60}$–$\mathrm{ZnTPPS}^{4-}$ and (b) $\mathrm{Li}^{+}@\mathrm{C}_{60}$–$\mathrm{H_2TPPS}^{4-}$ nanoclusters.

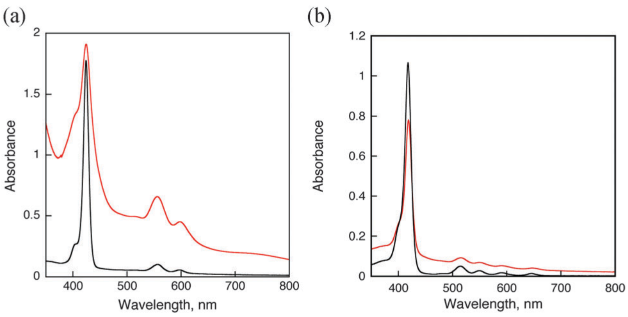


Fig. 1 UV-vis absorption spectra of PhCN solutions of MTPPS^{4-} (black) and electrodes of OTE/$\mathrm{SnO_2}$–$(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ (red), M = (a) Zn and (b) $\mathrm{H_2}$.

Photoelectrochemical measurements were performed using a standard two-electrode system consisting of a working electrode and a Pt wire gauze electrode in air-saturated MeCN containing 0.5 M LiI and 0.01 M $\mathrm{I_2}$ (Scheme 1). In order to evaluate the response towards the photocurrent generation, a series of photocurrent action spectra were recorded. The IPCE (incident photon-to-photocurrent efficiency) values were calculated by normalizing the photocurrent values for incident light energy and intensity and using eqn (1),[12]

$$\mathrm{IPCE}\ (\%) = 100 \times 1240 \times i_{\mathrm{sc}}/(I_{\mathrm{inc}} \times \lambda) \qquad (1)$$

where i_{sc} is the short circuit photocurrent (A cm^{-2}), I_{inc} is the incident light intensity (W cm^{-2}) and λ is the wavelength (nm). The maximum IPCE values of OTE/$\mathrm{SnO_2}$–$(\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ (black spectrum in Fig. 3a) and OTE/$\mathrm{SnO_2}$–$(\mathrm{ZnTPPS}^{4-})_n$ (blue spectrum) are only 5% (425 nm) and 22% (445 nm), respectively. In contrast to the reference experiments, the IPCE value of OTE/$\mathrm{SnO_2}$–$(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ is much higher than the sum of the two individual IPCE values of the individual systems OTE/$\mathrm{SnO_2}$–$(\mathrm{ZnTPPS}^{4-})_n$ and OTE/$\mathrm{SnO_2}$–$(\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ in the visible region. The maximum IPCE value attained in these experiments was 77% at 450 nm. The high ICPE value at the Q-band region was also observed to be 50% at 570 nm. Such a high IPCE value indicates that photocurrent generation is initiated *via* photoinduced electron transfer in supramolecules between ZnTPPS^{4-} and $\mathrm{Li}^{+}@\mathrm{C}_{60}$, followed by the charge transport to the collective surface of the OTE/$\mathrm{SnO_2}$ electrode (Scheme 1). When ZnTPPS^{4-} was replaced by $\mathrm{H_2TPPS}^{4-}$, a significantly low IPCE value of 7% was observed at 440 nm (Fig. 3b) probably because of the self-aggregation of $\mathrm{H_2TPPS}^{4-}$ without binding with $\mathrm{Li}^{+}@\mathrm{C}_{60}$.[13]

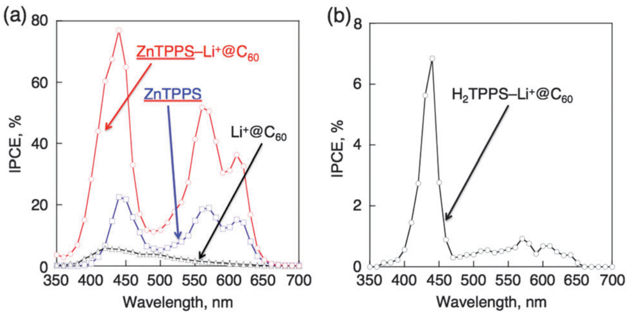


Fig. 3 Photocurrent action spectra of (a) OTE/$\mathrm{SnO_2}$–$(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ (red), OTE/$\mathrm{SnO_2}$–$(\mathrm{MTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ (blue) and OTE/$\mathrm{SnO_2}$–$(\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ (black) and (b) OTE/$\mathrm{SnO_2}$–$(\mathrm{H_2TPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$. Electrolyte: 0.5 M LiI and 0.01 M $\mathrm{I_2}$ in MeCN–PhCN (3 : 1 v/v).

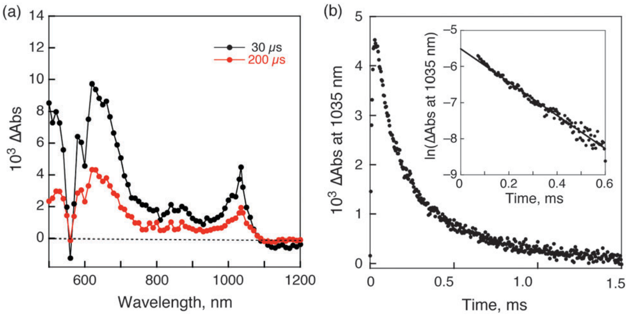


Fig. 4 (a) Transient absorption spectra of $(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ in deaerated MeCN–PhCN (3 : 1 v/v) taken at 30 μs (black) and 200 μs (red) after laser excitation at 550 nm. (b) Time profile at 1035 nm. Inset: first-order analysis.

We have also evaluated the power characteristics of the OTE/SnO_2–$(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ electrode (Fig. S2 in the ESI†). The power conversion efficiency, η, is calculated using eqn (2):[12]

$$\eta = FF \times I_{\mathrm{sc}} \times V_{\mathrm{oc}}/W_{\mathrm{in}} \tag{2}$$

in which the fill factor (FF) is defined as $FF = [IV]_{\max}/I_{\mathrm{sc}}V_{\mathrm{oc}}$, and V_{oc} is the open-circuit photovoltage and I_{sc} is the short-circuit photocurrent. OTE/SnO_2–$(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ has a an overall η value of 2.1% at an input power (W_{in}) of 28 mW cm^{-2}, whereas $FF = 0.37$, $V_{\mathrm{oc}} = 460$ mV and $I_{\mathrm{sc}} = 3.4$ mA cm^{-2} in the OTE/SnO_2–$(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$. Note that the η value is two orders of magnitude greater than that of the previously reported simple porphyrin and C_{60} composite system (∼0.03%).[12] Such a significant enhancement of the η value demonstrates that the strong ordering in the clusters and the efficient charge separation in $(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ improved the light energy conversion properties.

In order to clarify the photocurrent generation mechanism, we examined formation of the CS state $[(\mathrm{ZnTPPS}^{4-})^{\bullet+}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}]$ by nanosecond laser flash photolysis measurements. Time-resolved transient absorption spectra of $(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ dispersed in a deaerated MeCN–PhCN solution (3 : 1 v/v) are shown in Fig. 4a, which clearly exhibit a broad absorption band at around 1035 nm.[8,9] This is diagnostic of formation of $\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}$ upon laser irradiation. Thus, photoinduced electron transfer occurs from ZnTPPS^{4-} to $\mathrm{Li}^{+}@\mathrm{C}_{60}$ in the composite cluster to produce the CS state $[(\mathrm{ZnTPPS}^{4-})^{\bullet+}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}]$. The absorption time profile of $[(\mathrm{ZnTPPS}^{4-})^{\bullet+}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}]$ recorded at 1035 nm is shown in Fig. 4b. The first-order decay kinetics (inset of Fig. 4b) corresponds to back electron transfer from $\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}$ to $(\mathrm{ZnTPPS}^{4-})^{\bullet+}$, affording a rate constant of back electron transfer $k_{\mathrm{BET}} = 4.6 \times 10^3\ \mathrm{s}^{-1}$. The lifetime of the CS state is 220 μs, which is long enough to inject an electron from $\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}$ of the CS state to the SnO_2 electrode before the charge recombination. Such a long-lived CS state was further detected by EPR under photoirradiation of an MeCN–PhCN solution (1 : 3 v/v) containing $(\mathrm{ZnTPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ at 77 K. The EPR signal was observed at $g = 2.0020$, which is attributable to the mixture of the porphyrin radical cation ($g = 2.002$)[14] and $\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}$ ($g = 2.0014$) (see Fig. S3a in the ESI†).[15] When ZnTPPS^{4-} was replaced by $\mathrm{H}_2\mathrm{TPPS}^{4-}$, the transient absorption bands due to the CS state was significantly smaller than the case of ZnTPPS^{4-} (Fig. S4, ESI†). This is the reason why the IPCE value of OTE/SnO_2–$(\mathrm{H}_2\mathrm{TPPS}^{4-}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60})_n$ was low as shown in Fig. 3b.

Based on the above-mentioned results, the photocurrent generation is initiated by photoinduced electron transfer from ZnTPPS^{4-} to $\mathrm{Li}^{+}@\mathrm{C}_{60}$ in the cluster to produce the CS state, $(\mathrm{ZnTPPS}^{4-})^{\bullet+}\text{–}\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}$. The reduced $\mathrm{Li}^{+}@\mathrm{C}_{60}$ ($\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}$) ($E(\mathrm{Li}^{+}@\mathrm{C}_{60}/\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}) = 0.14$ V *vs.* SCE)[8,9] injects electrons into the conduction band of SnO_2 (0.2 V *vs.* SCE),[11] whereas the oxidized ZnTPPS^{4-} ($E(\mathrm{ZnTPPS}^{4-}/(\mathrm{ZnTPPS}^{4-})^{\bullet+}) = 0.74$ V *vs.* SCE)[8] undergoes the electron-transfer reduction with the iodide ($\mathrm{I}_3{}^{-}/\mathrm{I}^{-} = 0.7$ V *vs.* SCE)[12] in the electrolyte solution.

In conclusion, the photoinduced electron transfer from ZnTPPS^{4-} to $\mathrm{Li}^{+}@\mathrm{C}_{60}$ in the supramolecular cluster makes it possible to enhance the performance of the photoelectro-chemical cell. Thus, the use of $\mathrm{Li}^{+}@\mathrm{C}_{60}$ as an electron acceptor in the supramolecular clusters with ZnTPPS^{4-} paves a new way for the design of high performance solar cells.

This work was supported by Grant-in-Aids for Scientific Research (No. 23750014 to K.O.; No. 23108721 & 23681025 to T.H.; No. 20108010 to S.F.), the Science Research Promotion Fund from the Promotion and Mutual Aid Corporation for Private Schools from MEXT, Japan, and a WCU project (R31-2008-000-10010-0) through KOSEF/MEST, Korea.

References

1 (*a*) M. Grätzel, *Nature*, 2003, **421**, 586; (*b*) M. Grätzel, *Nature*, 2001, **414**, 338; (*c*) B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
2 (*a*) A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49; (*b*) A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, 2000, **33**, 269.
3 (*a*) W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425; (*b*) A. Shah, P. Torres, R. Tscharner, N. Wyrsch and H. Keppner, *Science*, 1999, **285**, 692.
4 *The Photosynthetic Reaction Center*, ed. J. Deisenhofer and J. R. Norris, Academic Press, San Diego, 1993.
5 (*a*) T. Hasobe, *Phys. Chem. Chem. Phys.*, 2012, **14**, 15975; (*b*) H. Imahori and S. Fukuzumi, *Adv. Mater.*, 2001, **13**, 1197.
6 (*a*) M. Lahav, V. Heleg-Shabtai, J. Wasserman, E. Katz, I. Willner, H. Dürr, Y.-Z. Hu and S. H. Bossmann, *J. Am. Chem. Soc.*, 2000, **122**, 11480; (*b*) J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov and G. Hadziioannou, *J. Am. Chem. Soc.*, 2000, **122**, 7467.
7 S. Fukuzumi and D. M. Guldi, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, Weinheim, 2001, vol. 2, pp. 270–337.
8 K. Ohkubo, Y. Kawashima and S. Fukuzumi, *Chem. Commun.*, 2012, **48**, 4314.
9 (*a*) S. Fukuzumi, K. Ohkubo, Y. Kawashima, D. S. Kim, J. S. Park, A. Jana, V. M. Lynch, D. Kim and J. L. Sessler, *J. Am. Chem. Soc.*, 2011, **133**, 15938; (*b*) Y. Kawashima, K. Ohkubo and S. Fukuzumi, *J. Phys. Chem. A*, 2012, **116**, 8942; (*c*) T. Kamimura, K. Ohkubo, Y. Kawashima, H. Nobukuni, Y. Naruta, F. Tani and S. Fukuzumi, *Chem. Sci.*, 2013, **3**, 1451.
10 H. Nobukuni, F. Tani, Y. Shimazaki, Y. Naruta, K. Ohkubo, T. Nakanishi, T. Kojima, S. Fukuzumi and S. Seki, *J. Phys. Chem. C*, 2009, **113**, 19694.
11 T. Hasobe, H. Imahori, S. Fukuzumi and P. V. Kamat, *J. Phys. Chem. B*, 2003, **107**, 12105.
12 T. Hasobe, Y. Kashiwagi, M. A. Absalom, J. Sly, K. Hosomizu, M. J. Crossley, H. Imahori, P. V. Kamat and S. Fukuzumi, *Adv. Mater.*, 2004, **16**, 975.
13 H. Matsuzawa, H. Kobayashi and T. Maeda, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 774.
14 S. Fukuzumi, K. Saito, K. Ohkubo, T. Khoury, Y. Kashiwagi, M. A. Absalom, S. Gadde, F. D'Souza, Y. Araki, O. Ito and M. J. Crossley, *Chem. Commun.*, 2011, **47**, 7980.
15 $\mathrm{Li}^{+}@\mathrm{C}_{60}{}^{\bullet-}$ was prepared by the electron transfer from dimeric 1-benzyl-1,4-dihydronicotinamide to $\mathrm{Li}^{+}@\mathrm{C}_{60}$,[9a] which was observed at 100 K by ESR (see Fig. S3b in the ESI†).