Vol. 50 Commemorative Highlight Review Polariton Chemistry in Cavity Vacuum Fields

Kenji Hirai^{*1,2} and Hiroshi Uji-i^{1,3}

¹Division of Photonics and Optical Science, Research Institute for Electronic Science (RIES), Hokkaido University, North 20 West 10, Kita ward, Sapporo, Hokkaido 001-0020, Japan ²Precursory Research for Embryonic Science and Technology (PRESTO),

Japan Science and Technology Agency (JST),

4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

³Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Leuven, Belgium

E-mail: hirai@es.hokudai.ac.jp



Kenji Hirai received his PhD from Kyoto University in 2013. He was a postdoctoral researcher at the University of Michigan. In 2014, he became a specially-appointed assistant professor at Hokkaido University, where he has been an associate professor since 2017. Since 2018, he has also been a researcher for PRESTO program of JST. His research interests are light-matter strong coupling and nanomaterials.



Hiroshi Uji-i received his PhD at the Department of Chemistry, Tohoku University in 2002. He was a postdoctoral researcher at KU Leuven. He was also the PRESTO researcher from 2009 to 2012. He is a research professor at KU Leuven, Belgium and professor at Hokkaido University, Japan. His research interests are nanoscopy and plasmonics.

Abstract

Even without external photon pumping, cavity vacuum fields can be strongly coupled with molecular transitions (electronic excitation and molecular vibration), resulting in the formation of polaritonic states. The energy states of molecular systems are altered under strong coupling, revealing intriguing phenomena, such as improvements in energy/exciton transfer and modulation of chemical reactions. In this review, we highlight recent advances in cavity strong coupling, including exciton strong coupling and vibrational strong coupling, from a chemistrybased viewpoint.

Keywords: Strong coupling | Rabi splitting | Fabry-Pérot cavity

1. Introduction

Quantum systems fluctuate in the lowest energy state, as explained by the Heisenberg uncertainty principle. Molecules can interact with an electromagnetic field at its lowest energy state, i.e., a vacuum field fluctuation. The use of a Fabry–Pérot (FP) cavity allows for the strong coupling of vacuum fields and molecules.^{1,2} The strong coupling between FP cavity modes and

molecular transitions (i.e., electronic excitation and molecular vibration) results in the formation of polaritonic states.³ These polaritonic states are generally separated into upper and lower branches, called vacuum Rabi splitting. It is noteworthy that the strong coupling between the vacuum field of an FP cavity and a molecular transition occurs even without external photon pumping.⁴ This is a characteristic feature that differentiates this phenomenon from other strategies for strong coupling, such as surface-plasmon polaritons.⁵

Whilst strong light–matter coupling has been known for half a century, strong coupling in molecular chemistry began to be explored only in the last decade. Recent studies on light–matter strong coupling have revealed intriguing phenomena that may have applications in both chemistry and materials science. For instance, strong coupling of an exciton (electron-hole pair) and a photon in an optical cavity generates polaritonic states that allow efficient energy/exciton transfer.^{6,7} Furthermore, the photoisomerization of functional molecules can be modulated under exciton–photon coupling.^{8,9} Another aspect that has recently emerged in this field is the modulation of reaction kinetics.^{10–15} Strong coupling can be further extended to molecular vibrations, termed vibrational strong coupling (VSC). The rates of organic



Figure 1. Applications of cavity strong coupling

reactions can be either increased or decreased under VSC. The modulation of chemical reactivity in organic reactions under VSC enables site-specific reactions by changing the reactivity of specific functional groups.¹⁶

In the initial stages, the field of strong coupling was developed by quantum physicists. However, considerable progress in strong coupling in molecular systems has extended the research in this field to chemistry. The field of strong coupling and its application to molecular chemistry is of high interest; this is because the phenomena that occur in cavity vacuum fields are counterintuitive for most chemists. In this review, we describe the emergence of a new cross-disciplinary area between molecular chemistry and cavity quantum electromagnetic dynamics (Figure 1).

2. Strong Coupling with Cavity Fields

FP cavities have been used to bring about the strong coupling of molecular transitions with cavity fields. An FP cavity comprises a set of reflection mirrors. A metal (e.g., Au, Ag, or Al) is deposited on a substrate by sputtering to fabricate the reflection mirrors. For the strong coupling of liquid samples. the metallic mirror is covered by an inert layer, such as resins, organic polymers or silicon dioxide, to avoid exposure to the molecules. The two inert mirrors are arranged such that they are parallel and face each other. The polymer films (e.g., Mylar or Kapton films) are often employed as spacers between the two mirrors. The thickness of the spacer films roughly determines the mirror separation and hence the resonant wavelength of the FP cavity. To tune the resonance wavelength to the targeted transition energy, the spacer film in the FP cavity is compressed with screws. A liquid sample is then introduced into the FP cavity to undergo strong coupling.

The spin coating of polymers containing functional molecules is also employed for strong coupling. To fabricate the metallic mirrors, a layer of metal is first deposited on a glass or quartz substrate via sputtering. A polymer solution containing the functional molecules is then spin-coated onto the mirror to form a smooth polymer film. After the spin coating, a second layer of metal is deposited on top of the polymer film, so that the polymer film is sandwiched between two metallic layers, thereby producing an FP cavity. The presence of functional molecules in the polymer layer forms a strong coupling regime. Because the mirror separation is determined by the thickness of the polymer film, the resonant wavelength can be adjusted to the targeted molecular transition by varying the thickness of the polymer film, which is controlled by changing the rotational speed of the spin coating or the concentration of the polymer solution.

2.1 Exciton Strong Coupling. Nearly half a century ago, strong exciton-photon coupling was experimentally observed.¹⁷ This phenomenon was interpreted based on the Jaynes and Cummings model.¹⁸ After the discovery of strong excitonphoton coupling, inorganic semiconductors^{19,20} and Rydberg atoms^{21,22} were extensively studied. Considerable research has been conducted on inorganic materials: however, strong exciton-photon coupling of organic molecules was only observed twenty years after the discovery of strong exciton-photon coupling.²³ Interest in the strong coupling of organic molecules has rapidly grown because of the large transition dipole moments of Frenkel excitons.^{24,25} The large transition dipoles of organic molecules enable a coupling strength greater than that of the Wannier-Mott excitons of inorganic materials. Because of these large transition dipole moments and binding energies, the strong coupling of organic molecules can be investigated at room temperature.

2.2 Vibrational Strong Coupling. Light-matter strong coupling is applied not only to electronic transitions. When the cavity mode is resonant with a vibrational transition, polaritonic states are formed. In 2015, VSC was experimentally observed for the first time (Figure 2).²⁶ The carbonyl stretching vibration of polyvinyl acetate was strongly coupled to the vacuum field in an FP cavity. The vacuum Rabi splitting derived from the VSC of the carbonyl stretching vibration was clearly observed via infrared spectroscopy. The VSC of organic molecules with various functional groups (carbonyl, azide, and cyano groups, carbon-carbon double bonds, and hydroxyl groups) has since been demonstrated.²⁷⁻³¹ The VSC of molecules dissolved in solvent inspired the investigation of the effect of VSC on solution-based reactions. To date, the VSC of various molecules, including organic polymers, organometallic complexes, proteins, and liquid crystals, has been reported. The use of VSC is likely to make a substantial contribution to molecular chemistry because of the wide variety of molecular systems that can be used with VSC.



Figure 2. IR transmittance of the coupled cavity (black line) and theoretical fit (red line). The dashed blue line indicates the C=O stretching vibrational mode of polyvinyl acetate. The formation of upper (UP) and lower polaritons (LP) was observed from the splitting of spectral peaks. This figure is reproduced from ref 26 with permission from Springer Nature.

3. Polaritonic Chemistry

3.1 Exciton Strong Coupling for Energy/Exciton Transfer. When the electronic transitions of organic dyes are coupled to cavity modes, the energy levels of absorption and emission are shifted because of the formation of polaritonic states. For instance, the strong coupling of a cavity mode and rhodamine 6G increased the Stokes shift between the emission and excitation maxima.³² This method of controlling the excitation states of organic dyes can be applied for efficient energy transfer. When the acceptor and donor molecules are simultaneously coupled to the cavity mode, a hybrid polaritonic state is formed. These hybrid states provide an efficient pathway for energy transfer between molecules that are far apart. Polaritonenhanced energy transfer was first observed in J-aggregated molecular dyes. Two kinds of J-aggregated dyes (NK-2707 and TDBC) embedded in a polymer matrix were placed in an FP cavity.6 The separation of the TDBC (donor) and NK-2707 (acceptor) was large enough to avoid direct energy transfer between them. The angle-dependent luminescence showed three branches: upper, middle, and lower branches. Analysis of the three polariton branches by a coupled oscillator model revealed hybridization of the molecular transitions of TDBC and NK-2707. A sevenfold increase in the energy transfer between two J-aggregated cvanine dyes (TDBC and BRK) under strong coupling has also been reported. Interestingly, the polaritonenhanced energy transfer occurred even if the donor and acceptor dyes were separated by a polymer layer.⁷ Owing to the delocalized polaritonic states, the transfer efficiency can reach 37% at donor-acceptor distances of over 100 nm, distances far greater than those reached with the Förster resonance energy transfer (FRET) mechanism. The energy transfer was independent of the distance, as far as the coupling strength was retained (Figure 3).

Organic light-emitting diodes (OLEDs) employ reversed intersystem crossing (RISC) to collect light from triplet states. RISC is inherently slow; thus, an increase in the rate of RISC enhances the performance of OLEDs. The excited singlet state of erythrosin B was coupled to the vacuum cavity mode, generating new polaritonic states.³³ The energy gap between the triplet and singlet states was reduced because of the formation of



Figure 3. Schematic illustration of cascade strong coupling. The cavity mode is coupled to the excited state of a donor, forming upper and lower polaritons, denoted as P+ and P-, respectively. The lower polariton (P-) is further coupled to the excited state of an acceptor, generating three polaritonic states: the upper (UP), middle (MP), and lower (LP) states.

polaritonic states. This reduction in the energy gap of the tripletsinglet states enhanced the rate of the RISC, resulting in a fourfold enhancement of the triplet decay rate.

Singlet fission (SF) is a phenomenon in which a singlet exciton is split into two triplet excitons via a triplet pair state. SF is often observed in amorphous rubrene. To investigate the effect of strong coupling on SF, a film of rubrene was sandwiched between two silver mirrors to couple the cavity mode with a singlet exciton of rubrene.³⁴ The dynamics of SF were strongly affected by the formation of the lower polariton. The LP equilibrium was shifted to the ground state by polaron decoupling, in which potential energy is displaced to reduce the reorganization energy in electronically excited states. Polaron decoupling under strong coupling regimes had been theoretically predicted, but this result provided experimental evidence of the pivotal role of polaron decoupling in SF.

The behavior of triplet excitons under strong coupling was further investigated. The spin-allowed conversion of two triplets into a single exciton is known as triplet-triplet annihilation. One of the best-known examples of triplet-triplet annihilation is one that occurs with photon up-conversion in a mixture of diphenylanthracene and Pt-porphyrin. A polystyrene film containing a mixture of diphenylanthracene and Pt-porphyrin was sandwiched between Ag reflecting mirrors acting as an FP cavity.³⁵ The S₁ state of diphenylanthracene was coupled to the cavity mode, forming polariton states. In this strong coupling regime, the emission always originated from the lower branch, whether the coupled diphenylanthracene or the uncoupled Ptporphyrin was excited. The lifetime of the emission from the strong coupling states was distinctly longer than that for uncoupled blends of diphenvlanthracene and Pt-porphyrin. The reason for the longer lifetime of the emission from the lower branch is still under discussion. Interestingly, this behavior could improve the quantum efficiency of photon up-conversion.

Exciton strong coupling also influences the transport of excitons. The charge carriers and excitons of organic molecules are localized on the individual molecules owing to the strong exciton binding energy. Generally, charge carriers and excitons migrate between molecules at room temperature by a hopping mechanism. A polariton (a hybrid state of photon and exciton) possesses the properties of a photon and delocalizes over the length of light. The transport of polaritons in organic materials can be more efficient than that of excitons. Therefore, the strong coupling of exciton and photon improves the migration of excitons and charge carriers in organic materials. The long-range migration of cavity polaritons in J-aggregates has been observed by ultrafast time-resolved microscopy.³⁶ The spectra showed that strong coupling between a cavity mode and molecules induced the long-range migration of excitons and propagation over several microns.

3.2 Exciton Strong Coupling for Photoisomerization. The photoisomerization of spiropyran to merocyanine was investigated under strong coupling in an FP cavity. By strong coupling of the excited state of spiropyran and cavity modes, two polaritonic states—lower and upper branches—were generated. The structural transformation between spiropyran and merocyanine becomes slower under the strong coupling because the lower polariton possesses lower energy than that of the uncoupled excited state. Thus, spiropyran must overcome the larger energy barrier for photoisomerization from the lower



Figure 4. (a) The molecular structure of merocyanine (MC) and spiropyran (SP). (b) Energy diagram of SP and MC under strong coupling. The excited state of MC was coupled to the cavity mode, thus forming two polaritonic states (P+ and P-). An energy barrier was formed from P- to the intermediate state (I).

polariton branch to the activated state, thus slowing down the structural transformation. This observation suggests that the energy landscape is altered by strong coupling in an optical cavity (Figure 4). Photoisomerization under strong coupling has been theoretically investigated for azobenzene. The change of kinetics in the photoisomerization was explained based on the formation of a polaritonic conical intersection in the strong coupling regime.⁹

3.3 VSC for Chemical Reactions. The effect of VSC on an organic reaction was first observed in the deprotection of an alkylsilane. The reactant (1-phenyl-2-trimethylsilylacetylene) was placed in an FP cavity to achieve VSC of the Si–C stretching vibration.¹⁰ The deprotection of 1-phenyl-2-trimethyl-silylacetylene was performed with tetra-*n*-butylammonium fluoride (TBAF). The reaction rate decreased by a factor of up to 5.5 under the VSC of the Si–C stretching vibration. Eyring plots of the reactions with and without VSC indicated a change in the reaction pathway. The deprotection of Si–C with TBAF generally begins by an associative reaction pathway, where a fluoride ion attacks the silicon atom to form an intermediate. Under VSC of the Si–C stretching vibration, however, the Si–C bond begins to break before the fluoride attacks the silicon center.

By utilizing the deacceleration of the Si–C deprotection reaction, site-selective deprotection of Si–O and Si–C bonds was realized.¹⁶ The reaction of a compound with two possible silyl bond cleavage sites, Si–C and Si–O bonds, was investigated under VSC of the Si–C and Si–O vibrations. The selective deprotection of *tert*-butyldimethyl{[4-(trimethylsilyl)but-3-yn-1-yl]oxy}silane was achieved by suppressing the reactivity of specific sites under VSC.

The effects of VSC on ketones and aldehydes in Prins cyclization reactions were also investigated. The reaction rate of the Prins cyclization reaction was diminished under VSC of the

 Table 1. Activation enthalpy, entropy, and energies of Prins cyclization under ON- and OFF-resonance.

State	ΔH [‡] [kJ mol ⁻¹]	Δ <i>S</i> [‡] [J mol ⁻¹ K ⁻¹]
OFF-resonance	19.2	-251.1
ON-resonance	30.9	-222.7
OFF-resonance	23.4	-240.7
ON-resonance	37.6	-204.7
OFF-resonance	25.0	-236.5
ON-resonance	36.8	-209.9
OFF-resonance	27.1	-231.7
ON-resonance	38.8	-205.6
	State OFF-resonance ON-resonance OFF-resonance OFF-resonance ON-resonance OFF-resonance	StateΔH* [kJ mol ⁻¹]OFF-resonance19.2ON-resonance30.9OFF-resonance23.4ON-resonance37.6OFF-resonance25.0ON-resonance36.8OFF-resonance27.1ON-resonance38.8

carbonyl stretching vibration in aldehydes or ketones.³⁷ Eyring plot indicated an increase of 10 kJ/mol in the activation enthalpy (ΔH^{\ddagger}) and almost no change in the activation entropy (ΔS^{\ddagger}) . The linear correlation of ΔH^{\ddagger} versus ΔS^{\ddagger} suggested that the reaction mechanism was not altered under VSC, however, the energy barrier of the reaction was increased. The rate-limiting step of Prins cyclization is protonation of the carbonyl group and the attack of oxygen at the carbonyl carbon. This work suggests that VSC of the carbonyl stretching vibration can influence the nucleophilicity of carbonyl oxygens and the electrophilicity of carbonyl carbons (Table 1).

The overlap of the vibrational modes of reactants and solvents allows strong coupling to cavity modes even if the concentration of the reactants is low. The cooperative strong coupling of solvents and reactants has been observed in solvolysis reactions. The solvolysis of para-nitrophenyl acetate (PNPA) was performed with TBAF.¹⁴ TBAF dissolved in ethyl acetate (EtOAc) induced the breaking of the acyl bond. The cooperative coupling of the carbonyl stretching vibration in PNPA, as the reactant, and EtOAc, as the solvent, significantly increased the reaction rate. The ΔH^{\ddagger} value decreased, meaning that the energy of the intermediate state was lowered under VSC. The ΔS^{\ddagger} value also decreased because the intermediate state was more polar under VSC. The re-structuring of the solvent cage of the polar transition state also decreased the ΔH^{\ddagger} value. This result suggested that the VSC of solvent molecules can also influence solution-based reactions.

The VSC of O–H stretching in enzyme reactions in water could also be regarded as cooperative coupling.¹⁵ The activity of pepsin was investigated under the VSC of OH stretching of both pepsin and the solvent water molecules. The reaction rate of peptide hydrolysis was decreased, whilst no effect was observed in VSC of the bending vibration of OH. Because OH groups exist in both water (the solvent) and the active sites of pepsin, the VSC of OH stretching vibrations could influence both the active sites of pepsin and the solvation. Changes in the hydration properties of water under VSC would change the structure of pepsin, thereby altering the reactivity of the enzyme.

VSC in molecular chemistry has been further extended to material synthesis. The self-assembly of metal ions and organic ligands yields porous framework structures, termed metal-organic frameworks (MOFs).^{38–40} The same combination of metal ions and organic ligands can sometimes yield MOFs with different structures (i.e., polymorphism).⁴¹ The selectivity of

crystal structures is influenced by the properties of solvent molecules. An observation of the effect of VSC on the solvolysis reaction reveals that the solvation properties can be changed under VSC. The effect of VSC of solvent molecules on crystallization of MOFs was investigated in the pseudopolymorphism of zeolitic imidazolate frameworks (ZIFs).⁴² The selfassembly of Zn(II) and 2-methylimidazole results in dimorphic structures: ZIF-L and ZIF-8.^{43,44} ZIF-8 crystals were selectively formed under VSC of the OH stretching vibration, whilst the mixtures of ZIF-L and ZIF-8 were formed otherwise.⁴⁵ This result indicates that VSC can be used to modulate self-assembly and material synthesis. Although the fundamental mechanism of the effects on chemical reaction is still under intensive discussion, a series of experimental results attract considerable attention from theoretical physicists.

4. Summary

Strong coupling in a vacuum field is a sub-area of quantum photonics. Approximately ten years ago, the strong coupling of molecular transitions began to be used to change molecular properties, such as the energy landscape⁸ and energy transfer/ relaxation pathways.^{6,7} More recently, VSC has emerged as a new concept that can be aligned with molecular chemistry. Recent breakthroughs have shown that the VSC of organic molecules can change the nature of their reactions,^{10,11,37} including influencing site-selective chemical reactions¹⁶ and enzymatic reactions.¹⁵ The development of theoretical frameworks providing deeper understanding of VSC-related phenomena could lead to the design of new applications for VSC.⁴⁶⁻⁴⁸ As described in this review article, molecular chemistry in cavity vacuum fields is still in the early stages, but this concept is receiving increasing attention in various research areas. An influx of new viewpoints has ensured the rapid development of strong coupling and offers the possibility of the concept being used to pioneer new cross-disciplinary research.

This work was supported by PRESTO, JST (JPMJPR18TA).

References and Notes

- 1 T. W. Ebbesen, Acc. Chem. Res. 2016, 49, 2403.
- 2 M. Hertzog, M. Wang, J. Mony, K. Börjesson, *Chem. Soc. Rev.* 2019, 48, 937.
- 3 R. F. Ribeiro, L. A. Martínez-Martínez, M. Du, J. Campos-Gonzalez-Angulo, J. Yuen-Zhou, *Chem. Sci.* 2018, 9, 6325.
- 4 V. P. Zhdanov, Chem. Phys. 2020, 535, 110767.
- 5 N. J. Halas, S. Lal, W.-S. Chang, S. Link, P. Nordlander, *Chem. Rev.* 2011, 111, 3913.
- 6 D. M. Coles, N. Somaschi, P. Michetti, C. Clark, P. G. Lagoudakis, P. G. Savvidis, D. G. Lidzey, *Nat. Mater.* 2014, 13, 712.
- 7 X. Zhong, T. Chervy, L. Zhang, A. Thomas, J. George, C. Genet, J. A. Hutchison, T. W. Ebbesen, *Angew. Chem., Int. Ed.* 2017, *56*, 9034.
- 8 J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, T. W. Ebbesen, *Angew. Chem., Int. Ed.* **2012**, *51*, 1592.
- 9 J. Fregoni, G. Granucci, E. Coccia, M. Persico, S. Corni, *Nat. Commun.* 2018, 9, 4688.
- 10 A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Chervy, X. Zhong, E. Devaux, C. Genet,

J. A. Hutchison, T. W. Ebbesen, Angew. Chem., Int. Ed. 2016, 55, 11462.

- 11 H. Hiura, A. Shalabney, J. George, *ChemRxiv* 2018, doi:10.26434/chemrxiv.7234721.v4.
- 12 K. Hirai, J. A. Hutchison, H. Uji-i, *ChemPlusChem* 2020, 85, 1981.
- 13 A. Thomas, A. Jayachandran, L. Lethuillier-Karl, R. M. A. Vergauwe, K. Nagarajan, E. Devaux, C. Genet, J. Moran, T. W. Ebbesen, *Nanophotonics* **2020**, *9*, 249.
- 14 J. Lather, P. Bhatt, A. Thomas, T. W. Ebbesen, J. George, Angew. Chem., Int. Ed. 2019, 58, 10635.
- 15 R. M. A. Vergauwe, A. Thomas, K. Nagarajan, A. Shalabney, J. George, T. Chervy, M. Seidel, E. Devaux, V. Torbeev, T. W. Ebbesen, *Angew. Chem., Int. Ed.* 2019, 58, 15324.
- 16 A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux, C. Genet, J. Moran, T. W. Ebbesen, *Science* 2019, 363, 615.
- 17 V. A. Yakovlev, V. G. Nazin, G. N. Zhizhin, *Opt. Commun.* 1975, 15, 293.
- 18 E. T. Jaynes, F. W. Cummings, Proc. IEEE 1963, 51, 89.
- 19 C. Weisbuch, M. Nishioka, A. Ishikawa, Y. Arakawa, *Phys. Rev. Lett.* **1992**, *69*, 3314.
- 20 R. Houdré, C. Weisbuch, R. P. Stanley, U. Oesterle, P. Pellandini, M. Ilegems, *Superlattices Microstruct.* 1994, 15, 263.
- 21 Y. Kaluzny, P. Goy, M. Gross, J. M. Raimond, S. Haroche, *Phys. Rev. Lett.* **1983**, *51*, 1175.
- 22 M. G. Raizen, R. J. Thompson, R. J. Brecha, H. J. Kimble, H. J. Carmichael, *Phys. Rev. Lett.* **1989**, *63*, 240.
- 23 V. Agranovich, H. Benisty, C. Weisbuch, *Solid State Commun.* 1997, 102, 631.
- 24 D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, T. Virgili, S. Walker, D. M. Whittaker, *Nature* 1998, 395, 53.
- 25 D. G. Lidzey, D. D. C. Bradley, A. Armitage, S. Walker, M. S. Skolnick, *Science* 2000, 288, 1620.
- 26 A. Shalabney, J. George, J. Hutchison, G. Pupillo, C. Genet, T. W. Ebbesen, *Nat. Commun.* 2015, *6*, 5981.
- 27 J. George, A. Shalabney, J. A. Hutchison, C. Genet, T. W. Ebbesen, J. Phys. Chem. Lett. 2015, 6, 1027.
- 28 J. P. Long, B. S. Simpkins, ACS Photonics 2015, 2, 130.
- 29 S. R. Casey, J. R. Sparks, J. Phys. Chem. C 2016, 120, 28138.
- 30 R. M. A. Vergauwe, J. George, T. Chervy, J. A. Hutchison, A. Shalabney, V. Y. Torbeev, T. W. Ebbesen, *J. Phys. Chem. Lett.* 2016, 7, 4159.
- 31 M. Hertzog, P. Rudquist, J. A. Hutchison, J. George, T. W. Ebbesen, K. Börjesson, *Chem.—Eur. J.* 2017, 23, 18166.
- 32 E. K. Tanyi, H. Thuman, N. Brown, S. Koutsares, V. A. Podolskiy, M. A. Noginov, *Adv. Opt. Mater.* 2017, *5*, 1600941.
- 33 K. Stranius, M. Hertzog, K. Börjesson, *Nat. Commun.* 2018, 9, 2273.
- 34 S. Takahashi, K. Watanabe, Y. Matsumoto, J. Chem. Phys. 2019, 151, 074703.
- 35 D. Polak, R. Jayaprakash, T. P. Lyons, L. Á. Martínez-Martínez, A. Leventis, K. J. Fallon, H. Coulthard, D. G. Bossanyi, K. Georgiou, A. J. Petty, II, J. Anthony, H. Bronstein, J. Yuen-Zhou, A. I. Tartakovskii, J. Clark, A. J. Musser, *Chem. Sci.* 2020, *11*, 343.

- 36 G. G. Rozenman, K. Akulov, A. Golombek, T. Schwartz, *ACS Photonics* **2018**, *5*, 105.
- 37 K. Hirai, R. Takeda, J. A. Hutchison, H. Uji-i, *Angew. Chem., Int. Ed.* **2020**, *59*, 5332.
- 38 S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
- 39 H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* 2013, 341, 1230444.
- 40 K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem.*, *Int. Ed.* **2002**, *41*, 281.
- 41 N. Zhu, M. J. Lennox, T. Düren, W. Schmitt, *Chem. Commun.* 2014, 50, 4207.
- 42 H. Hayashi, A. P. Côté, H. Furukawa, M. O'Keeffe, O. M.

Yaghi, Nat. Mater. 2007, 6, 501.

- 43 Z.-X. Low, J. Yao, Q. Liu, M. He, Z. Wang, A. K. Suresh, J. Bellare, H. Wang, *Cryst. Growth Des.* **2014**, *14*, 6589.
- 44 Y. Lo, C. H. Lam, C.-W. Chang, A.-C. Yang, D.-Y. Kang, *RSC Adv.* 2016, 6, 89148.
- 45 K. Hirai, H. Ishikawa, J. A. Hutchison, H. Uji-i, *ChemRxiv* 2020, doi:10.26434/chemrxiv.13191617.v1.
- 46 J. Flick, H. Appel, M. Ruggenthaler, A. Rubio, J. Chem. Theory Comput. 2017, 13, 1616.
- 47 J. Flick, M. Ruggenthaler, H. Appel, A. Rubio, *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 3026.
- 48 J. A. Campos-Gonzalez-Angulo, R. F. Ribeiro, J. Yuen-Zhou, *Nat. Commun.* 2019, 10, 4685.