Water-Induced Tuning of the Emission of Polyaniline LEDs within the NIR to Vis Range

Jerzy J. Langer,* Katarzyna Ratajczak, Ewelina Frąckowiak, and Sebastian Golczak

ABSTRACT: Tuning of the emission within the near-infrared to visible range is observed in p-toluenesulfonic acid-doped polyaniline light emitting diodes (PANI/PTSA), when water molecules are absorbed by the active material (wet PANI/PTSA). This is a hybrid material that combines a conjugated \( \pi \)-electron system and a proton system, both strongly interacting in close contact with each other. The proton system successfully competes with the electron system in excitation energy consumption (when electrically powered), thanks to the inductive resonance energy transfer from electrons to protons in wet PANI/PTSA at the energy levels of combination of vibrations and overtones in water, with subsequent light emission. Wet PANI/PTSA, in which electrons and protons can be excited parallelly owing to fast energy transfer, may emit light in different ranges (on a competitive basis). This results in intense light emission with a maximum at 750 nm (and the spectrum very similar to that of an excited protonic system in water), which is blue-shifted compared to the initial one at \( \sim 850 \) nm that is generated by the PANI/PTSA dry sample, when electrically powered.

**INTRODUCTION**

Electron transfer, proton transfer, and excitation energy transfer from electrons to protons with excitation of the proton system are of great importance for key biological processes and modern advanced technological applications as both intramolecular processes and external, intermolecular, and intersystem ones. The last case is particularly interesting in connection to technical applications, but they also have a crucial role in functioning biological systems at cellular and sub cellular levels. Such complex problems and systems are very often successfully examined with experimental and theoretical models, supported by computer simulations.

A unique model material for studying some aspects of these processes by electroluminescence is p-toluenesulfonic acid-doped polyaniline (PANI/PTSA). This is due to the presence of a conjugated \( \pi \)-electron system with relatively high electrical conductivity and an interacting with it coupled hydrogen bonding system, which can be modified by the presence of water molecules (Figure 3a).

The emission of light by conductive polymers that are electrically powered has been of our interest for over 10 years using macroscopic samples \((\sim 1 \) mm) in experiments, instead of thin layers with a thickness of \( \sim 1 \) \( \mu \)m, unlike in other laboratories. We described polyaniline light-emitting diodes (LEDs) with non-linear effects, including stimulated Raman scattering and polyaniline lasing, and also the electroluminescence of polypyrrole.

On the other hand, we have discovered emission of light in the entire range of ultraviolet–visible–near-infrared (UV–vis–NIR) due to the excitation of protons in the protonic analogue of the p–n junction—protonic LED, formed in water as a protonic semiconductor, appropriately doped.

In this paper, we describe the unique light emission observed in polyaniline doped with p-toluenesulfonic acid (PANI/PTSA), which is modified (tuned) in the range from 850 nm (NIR) to 750 nm (vis) in the presence of water.

The emitter is a hybrid material that combines conjugated \( \pi \)-electrons and a coupled proton system, both strongly interact with each other, while remaining in close contact, so that electrons and protons can be simultaneously excited due to energy transfer, when the system is electrically powered.

**RESULTS AND DISCUSSION**

This work is devoted to unique properties of polyaniline doped with p-toluenesulfonic acid, PANI/PTSA, a hybrid model material, where electrons and protons are excited when electrically powered, emitting the light in different ranges in a competitive way. The curiosity is that the protonic system...
starts to be active (effective in emission) in the presence of water and it is competitive despite emitting the light of higher photon energy (blue-shifted). The final result resembles a photon upconversion—NIR emission transits into the vis range—but the mechanism is different.

The diode formed with dry polyaniline doped with p-toluenesulfonic acid (solid pressed pellet, with a thickness of 0.5 ± 0.01 mm and a diameter of 3 mm) emits mostly in NIR with a maximum at 840–885 nm (Figures 1 and 2a). This corresponds to the excitations of $\pi$-electrons and emission due to the charge-transfer (CT) processes in organic materials.\textsuperscript{20,27−29} Here, CT between PTSA and polyaniline and also between quinoid and aromatic moieties in polyaniline chains is to be considered, including the formation of polarons that are weakly emissive.\textsuperscript{30}

PTSA can interact with PANI in two ways:
- due to Coulomb forces of negative and positive charges of anionic $-\text{SO}_3^-$ and cationic $-\text{N}^+\text{H}^+$ groups, respectively (Figure 3a, TPSA2 and TPSA3);
- due to non-polar forces, originating from interactions of $\pi$-electron aromatic rings (Figure 3a, TPSA1), which are particularly adequate for the CT process; in addition, these are responsible for lowering the energy of the electron excited state and the energy of photons generated, leading to emission in the NIR region with a maximum at 845–885 nm; electroluminescence of PANI/HCl, polyaniline doped with HCl—with no $\pi$-electron interactions, is observed as broad bands at 460, 575, and 657 nm, with a maximum at 575 nm.\textsuperscript{21}

**Influence of Water.** With the increase in the water content (humidity of the active material—polyaniline doped with p-toluenesulfonic acid), a shift of the maximum emission toward the blue and an increase in the light intensity in a part of the spectrum around 750 nm are observed, while the emission intensity at 845–885 nm decreases clearly (Figures 1 and 2a,b). Generally, the high dielectric constant of water should result in a bathochromic shift of the emission,\textsuperscript{31} which is not observed. On the other hand, the observed blue shift of 100 nm is too large to be considered a typical hypsochromic effect related to the protonation of nitrogen atom $n$-electrons due to polyaniline hydration. In addition, there is no pure $n-\pi$ transition identified in polyaniline, and the spectral range considered corresponds to CT and polaron bands.\textsuperscript{31,32} This indicates another mechanism—an effective transfer of the excitation energy (originally provided by the electric current) from the electron system of polyaniline into the protonic one.\textsuperscript{3}

The energy transfer to the coupled protonic system\textsuperscript{37−39} is fast and effective enough so that the light emission from an excited protonic system\textsuperscript{3} takes place as a competitive process, which is similar in mechanism to the generation of polaritons owing to strong coupling, when the resonant energy exchange between a confined optical mode and a material transition is faster than any decay process.\textsuperscript{44} In consequence, the loss of energy is lower than in the case of the excited polyaniline electronic states. This results in a blue-shifted spectrum and more intensive light emission. In wet PANI/PTSA, owing to inductive resonance energy transfer (IRET) from electrons to protons, the provided electrical energy excites the protonic system up to the energy levels of combination vibrations and overtones in water-coupled hydrogen bonding\textsuperscript{3,24} with subsequent emission of light at 750 nm. This is a unique behavior. Usually, the hydrogen bonding system is responsible for the dissipation of the excitation energy due to the rapid energy transfer between the electron and proton systems, followed by the energy flow in the hydrogen bonding network, and consequently the relaxation of electronic excitations through conjugated hydrogen bonds.\textsuperscript{3,33−37}

**Dissipation and Transfer of the Excitation Energy.** The light emission from the protonic system excited owing to IRET from electrons to protons is a new phenomenon, which dominates in experiments performed with wet PANI/PTSA (Figure 2a,b). The emission spectrum consists of two components: the contribution of the excited basic electron system of dry PANI/PTSA with a maximum at $\approx 850$ nm and the excited protonic system (including water) at $\approx 750$ nm in wet PANI/PTSA, which are additive in a competitive way (Figures 1 and 2a,b). In both cases, despite the emission of light, the dissipation of the excitation energy also takes place in non-radiative processes.\textsuperscript{3}

This is particularly effective when the electron and proton systems are involved at a comparable level in consuming the excitation energy, that is, for the emission amplitude ratio of A\textsubscript{750nm}/A\textsubscript{850nm} equal to 1 (Figure 2b). The proton system is not yet ready and effective enough in emission, but both channels dissipate the energy, leading to the lowest light emission.

Generally, in polyaniline, there is a strong coupling between electrons and protons, including the absorbance of water.\textsuperscript{31} Protonation essentially influences the PANI $\pi$-electron system and the electrical conductivity (e.g., emeraldine salt, Figure 3b). This enables efficient energy transfer and excitation...
Figure 2. Evolution of PANI/PTSA electroluminescence spectra with increasing water content: sample 1, 10.9% H₂O; sample 2, 14.4% H₂O; sample 3, 15.9% H₂O; sample 4, 17.1% H₂O; and sample 5, 17.7% H₂O (a). Changes in the spectral amplitudes of the emission at 750 and 850 nm (the emission at 750 nm is typical for wet PANI/PTSA and that at 850 nm corresponds to dry PANI/PTSA) as a function of the amplitude ratio of \( A_{750nm}/A_{850nm} \); the ratio \( A_{850nm}/A_{750nm} \) linearly correlates with the water content—inset (b).
the protonic system, when polyaniline electrons are excited owing to the electric current flow.

**Electrical Conductivity.** A well-defined emission from dry PANI/PTSA with the lowest quantum photon energy of 1.401 eV and a wavelength of 885 nm corresponds to the polaron band. The polyaniline used is a highly conductive material, mainly in the form of an emerald salt (Figure 3b) with an electrical conductivity of 0.8−3.8 S/cm (measured directly in our experiments) and a low energy gap of 0.3 eV, comparable to the data already published 0.2−0.5 eV. This corresponds to the Fourier-transform infrared (FTIR) absorption attributed to the electron transition—an intensive wide band centered at 1116 cm\(^{-1}\) (Figure 4). The optical energy gap corresponding to the vis−NIR emission spectrum of dry PANI/PTSA is higher and amounts to 1.934 eV. The pernigraniline fraction (Figure 3c) with a lower conductivity and a band gap of about 2 eV is expected to exist as domains that act as emission centers. The domain structure of polyaniline has been described previously. In our experiments, the high electrical conductivity of the polyaniline matrix is necessary to achieve the threshold emission current of 7.7 A at 3.04 V, followed by the operating current of 18 A (minimum) at 3.84 V (Figure 5).

**Stability of the Active Material.** Despite sudden changes in the current (and the electrical conductivity, e.g., 0.76, 3.8, and 1.05 S/cm—before, during, and after emission, respectively), the material stays relatively stable with respect to its electronic structure and electrical properties (Figure 5), including the characteristic parameters measured using the electron paramagnetic resonance (EPR). The EPR signals are very strong for all samples examined (Figure 6), which indicate a high concentration of polarons (dominating charge carriers in polyaniline). Each of the spectra consists of a single narrow Lorentzian line, with the asymmetric factor between 1.01 (dry PANI/PTSA) and 1.16 (wet PANI/PTSA). The values of g-factor lie in a narrow range from 2.00291 (wet PANI/PTSA) to 2.00291 (dry PANI/PTSA).

![Figure 3. Model of the PANI/PTSA complex; inset: wet PANI/PTSA (a), emeraldine base and emeraldine salt (b), and pernigraniline (c).](http://pubs.acs.org/journal/acsodf)
photons at 750 and 850 nm is electrically powered. The di ff erence in energy than an excited polyaniline supplied energy leads to the emission of photons of greater 

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dissipation. Polarons and bipolarons, generated in a polyaniline 

π-electron system (Figure 6) are non-light-emitting quasi-

particles,32 and energy can be dissipated by molecular vibration. On the other hand, excitation of a protonic system 

is efficient in light emission, as previously observed.24 There is a convincing similarity between the electroluminescence spectra of sulfonated polystyrene doped water 24 and the 

protonic system contribution at 750 nm in the current wet 

PANI/PTSA experiments (Figure 7). Thus, the process of 

exciting a protonic system and then emitting light is efficient 

and effectively competitive with the non-radiative energy 

dissipation from the excited electronic system of polyaniline. 

Due to the efficient electron-to-proton energy transfer and 

the excitation of the protonic system, less dissipation of the 

supplied energy leads to the emission of photons of greater 

energy than an excited polyaniline π-electron system, when 

electrically powered. The difference in the energy of the 

photons at 750 and 850 nm is \(-0.195 \text{ eV (0.19448 eV)}\), which 

corresponds to the excitation of molecular vibrations in 

polyaniline, for example, aromatic rings and quinoid grouping 

at \(\approx 1570 \text{ cm}^{-1}\).38–40 They have a strong influence on 

the electron energy (they partially absorb it and dissipate it) but 

are not involved in the excitation of the proton system, so the 

energy is not dissipated in this way after a fast transfer (Figure 

1), eventually leading to a blue shift in the emission spectrum 

in the presence of water (wet PANI/PTSA).

Changes in the emission spectrum (estimated roughly by the 

amplitude ratio at 850 and 750 nm) depend on the sample 

moisture (Figure 2). In this way, the emission spectrum can be 
made by gradually shifting the emission from the NIR to 

the vis range.

This process is expected to be particularly effective when 

using micro- and nanostructured light-emitting materials, as in 

our case (Figure 8c), due to the easy diffusion and good 

contact between water molecules and the active material— 

here, PANI macromolecules. The effect depends on the ability 

of the proton system (in water) to interact with the electron 

system, which is more effective for a micro- and nano-

structured material.

CONCLUSIONS

Fast transfer of excitation energy from π-electrons to protons 
in conjugated hydrogen bonds and effective excitation of the 

proton system in a hybrid material with strongly coupled 
electron and proton systems (wet PANI/PTSA) lead to 

emission of photons with higher energy than the π-electron 

system in dry PANI/PTSA, when the sample is electrically 

powered. The water proton system, incorporated into the wet 

PANI/PTSA, effectively competes with the electron system in 
terms of excitation energy consumption, resulting in blue-

shifted light emission due to lower energy dissipation. As the 

amount of water absorbed increases, the initial infrared 

emission at \(\approx 850 \text{ nm (NIR)}\) from the dry PANI/PTSA 

gradually shifts toward the vis range to reach \(\approx 750 \text{ nm for the} \) 
wet PANI/PTSA.

Apart from the possibility of tuning the emission spectrum, 
the fast and effective transfer of the excitation energy from 
the electron system to the proton system at the level of the 
overtones of fundamental oscillations in water molecules 
(regardless of the source of the excitation energy) is very 
important for basic biological processes3 and also for some 
modern technical applications, for example, water splitting for 

fuel production.7 This makes our results potentially even 

wider.
METHODOLOGY

Materials and Methods. Polyaniline was prepared by oxidation of aniline hydrochloride (10% in water at pH about 1) with the chemical method described elsewhere, modified in our laboratory.

The polymeric material (polyaniline) was characterized with physical and chemical methods: FTIR, EPR, elemental analysis, and electrical conductivity measurements, giving results similar to the values measured for materials previously prepared in our laboratory.\textsuperscript{21,22,45}

Chemicals and solvents:
- Hydrochloric acid (HCl) (Stanlab, pure p.a.)—600 mL of 1 M solution prepared from concentrated hydrochloric acid (36%)—50 mL of 36% HCl dissolved in 550 mL of H\textsubscript{2}O.
- Aniline hydrochloride (C\textsubscript{6}H\textsubscript{8}NCl) (Fisher Scientific, pure p.a.)—6.9 g of aniline hydrochloride dissolved in 300 mL of 1 M hydrochloric acid.
- Ammonium persulfate [(NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8}] (Chempur, pure p.a.)—11.4 g of ammonium persulfate was dissolved in 200 mL of 1 M hydrochloric acid.
- Ammonium hydroxide (NH\textsubscript{4}OH) solution 25% (POCh, pure p.a.)—500 mL of 1 M solution prepared from concentrated ammonium hydroxide (25%)—37 mL of 25% ammonium hydroxide dissolved in 463 mL of H\textsubscript{2}O.
- Chloroform (CHCl\textsubscript{3}) (Chempur, pure p.a.)—75 mL.
- p-Toluenesulfonic acid (CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}SO\textsubscript{3}H) (Aldrich, p.a.)—1.4 g of p-toluenesulfonic acid was dissolved in 75 mL of chloroform.

Pyrrole. Aniline hydrochloride (6.9 g) was dissolved in 300 mL of 1 M hydrochloric acid. At the same time, 11.4 g of ammonium persulfate was dissolved in 200 mL of 1 M hydrochloric acid (separately).

The ammonium persulfate solution was slowly added to a solution of aniline hydrochloride. The resulting dark-green solution was stirred with a magnetic stirrer at room temperature for 24 h.

Figure 5. Typical current and voltage changes as a function of time, recorded before (1), during (2), and after the emission (3) for dry PANI/PTSA; the dashed line shows the minimum operating voltage of 3.74 V and the current of 18 A.
Figure 6. EPR spectra of PANI/PTSA: (a) PANI/PTSA before experiments (powder), g-factor = 2.00292, line width $\Delta H$ [mT] = 0.285, asymmetry $A$ = 1.13; (b) crushed dry pellets of PANI/PTSA after light emission, g-factor = 2.00299, line width $\Delta H$ [mT] = 0.236, asymmetry $A$ = 1.01; and (c) crushed wet pellets of PANI/PTSA after light emission, g-factor = 2.00291, line width $\Delta H$ [mT] = 0.228, asymmetry $A$ = 1.16.
The precipitate was filtered under reduced pressure and washed several times with distilled water until the filtrate was nearly colorless and neutral. The solid product was treated with 500 mL of 1 M ammonium hydroxide and stirred with a magnetic stirrer at room temperature for 20 h.

The precipitate was isolated by filtration under reduced pressure and washed several times with distilled water until pH ~ 7. The dark-blue precipitate of the emeraldine base (PANIEB) was dried under ambient conditions (yield 1.8 g).

Elemental analysis:
Found [%]: C 74.05, H 5.01, N 13.61, O 7.33.
Figure 8. Sample examined (a) and its cross section observed by SEM (b); raw micro- and nanostructured PANI/PTSA, SEM image 5000×; inset: zoomed-in view (c).

Calculated [%]: C 72.69, H 5.09, N 14.13, O 8.07.
\[\left[\text{C}_6\text{H}_4\text{N}_2\text{H}_2\text{O}\right]_n\] where one molecule of H_2O is associated with two monomeric units of C_6H_4N.

Polyaniline Protonated with p-Toluenesulfonic Acid, PANI/PTSA. 1.4 g of p-toluenesulfonic acid was dissolved in 75 mL of chloroform. Then, 0.9 g of PANIEB was added to this solution in small portions. The mixture was stirred with a magnetic stirrer for 2 h. The dispersion was dripped into a beaker containing 200 mL of distilled water while stirring all the time. The precipitate was filtered under reduced pressure and washed several times with distilled water until pH ~ 4.5 has been obtained. To remove most water from the product, it was washed several times with methanol. The obtained polyaniline protonated with p-toluenesulfonic acid (PANI/PTSA) was dried for 24 h at room temperature.

Elemental analysis:
Found [%]: C 61.605, H 5.145, N 8.47, O 18.528, S 6.252.
Calculated [%]: C 60.450, H 5.280, N 8.46, O 19.330, S 6.070.

\[\left(\left[3\left(\text{C}_6\text{H}_4\text{N}_2\text{H}_2\text{O}\right)\cdot\text{C}_6\text{H}_4\text{SO}_3\right]\right)\] where three molecules of H_2O are associated with three monomeric units of C_6H_4N (1:1) and one unit of the acid: \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}.

FTIR spectra were measured as a suspension in KBr, pressed disc; for example, Figure 4 (B—benzenoid rings; Q—quinoid rings).

Elemental analyses were performed using a model Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany).

FTIR spectra were recorded using the spectrometer model IFS 66/s (Bruker, USA).

The EPR spectra were recorded using an EPR spectrometer model SE/X 2547 (RADIOPAN, Poland).

The emission UV−vis−NIR spectra were registered on-line with a Spectrometer model 2000 Ocean Optics PC2000 at a resolution of 0.5 nm at the same time when the current and the voltage were measured.

The beam profile was pictured directly with a digital camera: Pentax Kr 12.4 MP + 18–55 mm lens.

The measurements were performed under ambient conditions and in a dark room.

The samples, formed at a pressure up to 6000 kG/cm^2 as pellets with a thickness of 0.4–0.5 ± 0.01 mm and a diameter of 3 mm (Figure 8a), were placed in a measuring holder inside a glass tube with a wall thickness of 1–2 mm between two solid copper electrodes with a diameter of 4.5 mm (or one of 4.5 mm and the second of 3 mm) and a length of 25 mm.21–23 Despite being pressed, the material is microporous (Figure 8b), which allows it to absorb water in the case of preparation of wet PANI/PTSA samples by direct contact with distilled water within 24 h or less.

The voltage and the current were measured with an accuracy of at least of 0.1% using a Brymen digital multimeter, model BM859x (computer controlled), and a Metrahit Energy multimeter (computer controlled) with a precision standard resistor of 0.001 Ω for current measurements, respectively. Stabilized power supplies applied: INCO Z-3020—DC voltage source, adjustable between 0.1 and 30 V under a load current of 0–20 A, and INCO Z-5001—DC voltage source, adjustable between 0.1 and 500 V under a load current of 0–1 A.

To simultaneously register the light beam and the emission spectrum, the optical fiber of the spectrometer was mounted on the same side as the photocamera, in most cases parallel to the optical axis of the camera (another configuration was also used). The distance between the sample and the aperture of the optical fiber was 1–3 cm, and the camera was located at a distance of 15–20 cm.24

Author Contributions
K.R. was responsible for performing the experiments, data collection and partial interpretation; E.F. was responsible for performing the experiments, data collection and partial interpretation; S.G. was responsible for EPR spectra measurement and interpretation.

Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Sjulstok, E.; Olsen, J. M. H.; Solov'ev, I. A. Quantifying electron transfer reactions in biological systems: what interactions play the major role? Sci. Rep. 2015, 5, 18446.
(2) Bondarev, S. L.; Tikhonovich, S. A.; Knyukhstho, V. N.; Buganov, O. V.; Raichenok, T. F. Ultrafast Deactivation of Excitation Energy in Rutin and Quercetin via Electron and Proton Transfers. Ophthalmology 2017, 1, 42–43.
(3) Giorgadze, T. G.; Khutishvili, I. G.; Khuskivadze, T. B.; Melikishvili, Z. G.; Bregadze, V. G. The Phenomena of Light Radiation and Electron Excitation Energy Transfer in Hydrolysis Reactions and for Analysis of the Quality of DNA Double Helix. Adv. Tech. Biol. Med. 2017, 5, 1000215.
(4) Marais, A.; Adams, B.; Ringsmuth, S.; Pressler, M.; Gruber, J. M.; Hendriks, R.; Schuld, M.; Smith, S. H. L.; Sinayskij, I.; Krüger, T. P. J.; Petruccione, F.; van Grondelle, R. The future of quantum biology. J. R. Soc. Interface 2018, 15, 20180640.
(5) Dey, A.; Ghori, N.; Das, A.; Ghosh, H. N. Proton-Coupled Electron Transfer for Photoinduced Generation of Two-Electron Reduced Species of Quinone. J. Phys. Chem. B 2020, 124, 11165.
(6) Cukier, R. I.; Nocera, D. G. Proton-coupled electron transfer. Annu. Rev. Phys. Chem. 1998, 49, 337.
(7) Broess, K.; Trinkunas, G.; van der Weij-de Wit, C. D.; Dekker, J. P.; van Hoek, A.; van Amerongen, H. Excitation Energy Transfer and Charge Separation in Photosystem II Membranes Revisited. Biophys. J. 2006, 91, 3776.
(8) Cramer, W. A.; Knaff, D. B. Oxidation—Reduction; Electron and Proton Transfer. Energy Transduction in Biological Membranes; Springer Advanced Texts in Chemistry; Springer: New York, NY, 1990; Vol. 6.
(9) Ageeva, A. A.; Babenko, S. V.; Magin, I. M.; Plyusnin, V. F.; Kuznetsova, P. S.; Stepanov, A. A.; Vasilievsky, S. F.; Polyaev, N. E.; Doktorov, A. B.; Leshina, T. V. Stereoelectricity of Electron and Energy Transfer in the Quenching of (S,R)-Ketoprofen-(S)-2-Tryptophan Dyad Excited State. Int. J. Mol. Sci. 2020, 21, 5370.
(10) Alata, I.; Broquier, M.; Dedonder, C.; Marceca, E. Electronic excited state of protonated aromatic molecules: protonated Fluorene. Chem. Phys. 2012, 393, 25–31.
(11) Lennox, J. C.; Kurtz, D. A.; Huang, T.; Dempsey, J. L. Excited-State Proton-Coupled Electron Transfer: Different Avenues for Promoting Proton/Electron Movement with Solar Photons. ACS Energy Lett. 2017, 2, 1246.
(12) Berenbeim, J. A.; Boldissar, S.; Owens, S.; Hagmark, M. R.; Gao, G.; Sionti, F. M.; Cohen, T.; Bode, M. F.; Patterson, C. S.; de Vries, M. S. Excited state intramolecular proton transfer in hydroxyanthraquinones: Toward predicting fading of organic red colorants in art. Sci. Adv. 2019, 5, No. eaaw5227.
(13) Huang, X.; Vasiliev, C.; Hunter, C. N. Excitation energy transfer between monomolecular layers of light harvesting LH2 and LH1 reaction centre complexes printed on a glass substrate. Lab Chip 2020, 20, 2529.
(14) Kohler, B. Ultrafast photoinduced energy and charge transfer: concluding remarks. Faraday Discuss. 2019, 216, 564.
(15) May, V.; Kühl, O. Charge and Energy Transfer Dynamics in Molecular Systems; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2011.
(16) El-Daly, S. A.; El-Azim, S. A.; Elmekawy, F. M.; Elbaradei, B. Y.; Shama, S. A.; Asiri, A. M. Photophysical Parameters, Excitation Energy Transfer, and Photoactivity of 1,4-Bis(5-phenyl-2-oxazolyl)-benzene (POPOP) Laser Dye. Int. J. Photoenergy 2012, 2012, 458126.
water following resonant terahertz excitation. Sci. Adv. 2020, 6, No. eaay7074.

(39) Zhou, J.; Lin, S.; Zeng, H.; Liu, J.; Li, B.; Xu, Y.; Zhao, X.; Chen, G. Dynamic intermolecular interactions through hydrogen bonding of water promote heat conduction in hydrogels. Mater. Horiz. 2020, 7, 2936.

(40) John, A.; Mahadeva, S. K.; Kim, J. The preparation, characterization and actuation behavior of polyaniline and cellulose blended electro-active paper. Smart Mater. Struct. 2010, 19, 045011.

(41) Chauhan, N. P. S.; Ameta, R.; Ameta, R.; Ameta, S. C. Thermal and conducting behaviour of emeraldine base (EB) form of polyaniline (PANI). Indian J. Chem. Technol. 2011, 18, 118.

(42) Langer, J. J. A process leading to the domain structure of aniline black (polyaniline). Synth. Met. 1990, 36, 35.

(43) Boyer, M.-I.; Quillard, S.; Rebourt, E.; Louarn, G.; Buisson, J. P.; Monkman, A.; Lefrant, S. Vibrational Analysis of Polyaniline: A Model Compound Approach. J. Phys. Chem. B 1998, 102, 7382.

(44) Kaeek, M.; Damari, R.; Roth, M.; Fleischer, S.; Schwartz, T. Strong Coupling in a Self-Coupled Terahertz Photonic Crystal. ACS Photonics 2021, 8, 1881–1888.

(45) Langer, J. Unusual properties of the aniline black: Does the superconductivity exist at room temperature? Solid State Commun. 1978, 26, 839.