

1 Physically Cross-Linked Hydrogel Based on Phenyl-1,3,5-triazine: 2 Soft Scaffold with Aggregation-Induced Emission

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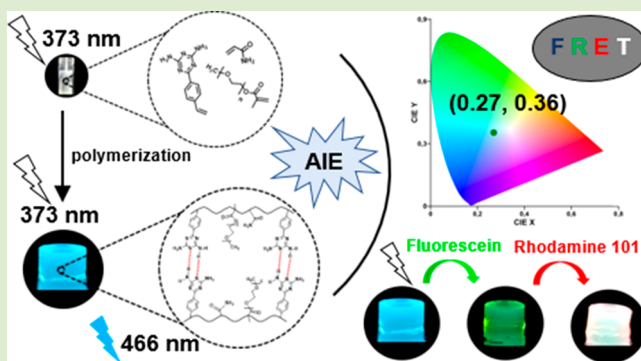
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8 **S** Supporting Information

9 **ABSTRACT:** A phenyltriazine compound has been used for
10 the first time as a monomer in the construction of a hydrogel.
11 This physically cross-linked soft material showed blue
12 fluorescence when excited under UV-light. Polymer formation
13 and intermolecular H-bonds arising from triazine moieties
14 operate as aggregation-induced emission (AIE) mechanisms.
15 The combination of soft materials and AIE properties expands
16 the applications of these materials. As a proof of concept, two
17 luminescent dyes have been incorporated into the hydrogel to
18 produce a white-light-emitting material.



19 **S**ince 2001, when Tang reported the aggregation-induced
20 emission (AIE) concept,¹ the interest in this phenomenon
21 has increased steadily. Nowadays, more than 4500 research
22 groups are involved in AIE studies, as summarized in a recent
23 special issue.² A large number of molecules, polymers,
24 dendrimers, and MOFs have been described as AIE-
25 luminogens (AIEgen) and they have been appropriately
26 reviewed.^{3–6} The presence of aromatic systems and their
27 restricted rotation are the most common features in AIE
28 structures. A huge number of interesting applications for
29 AIEgen have also been reported. Examples of biological
30 probes, chemical and biosensors, optoelectronics devices, and
31 smart materials have been extensively reviewed,^{5,7–10} along
32 with the recent use of AIE-fluorophores in solar concen-
33 trators.¹¹

34 A great deal of effort has been focused on establishing
35 mechanisms to explain this relatively new phenomenon.^{5,12}
36 Restriction of intramolecular rotations (RIR), restriction of
37 intramolecular vibrations (RIV), and restriction of intra-
38 molecular motions (RIM) have been proposed as the origins
39 of AIE. RIR is characteristic of molecules that adopt propeller-
40 type conformations that avoid packing of aromatic rings. This
41 phenomenon was observed for the first time by Chen et al. in
42 1,1-disubstituted-2,3,4,5-tetraphenylsiloles.¹³ RIV has been
43 shown to be the mechanism operating to explain AIE in
44 molecules that do not have rotatable units, such as
45 tetrabenzoheptafulvalene derivatives.¹⁴ In these cases, the
46 vibrational motions, unlike the rotational motions in the case
47 of RIR, are the origin of the exciton energy consumption. RIM

is used to describe the coexistence of both rotational and
vibrational restrictions in AIE molecules.^{15,16}

Hydrogels are three-dimensional (3D) polymeric networks
that are able to absorb aqueous solutions without dissolving.
This high water content imparts exceptional properties to these
materials, including flexibility, softness, and biocompatibility,
which make them suitable materials for biological applications
such as controlled drug delivery,¹⁷ tissue engineering, and
regenerative medicine¹⁸ or biosensors,¹⁹ among others.²⁰ The
three-dimensional structure of hydrogels is often maintained
through hydrogen bonds, van der Waals forces, or π - π and
dipole-dipole interactions (physically cross-linked hydrogels),
but it can also be sustained by covalent bonds (chemically
cross-linked hydrogels).

The AIE phenomenon has already been observed in
supramolecular gels^{15,21–24} formed by the self-assembly of
low molecular weight molecules, as well as polymer hydrogels
bearing archetypal luminogens in their structural design.^{25–30}
However, to the best of our knowledge, the existence of a
hydrogel with AIE properties resulting from the hydrogelation
process, and not as a consequence of the luminescent nature of
its single components, has not been described to date.

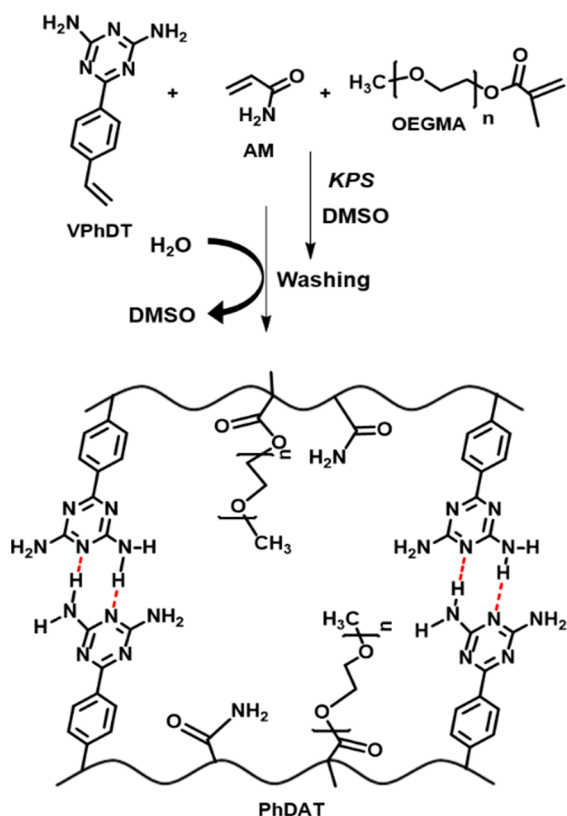
White-light-emitting materials have recently shown great
potential for lighting devices and sensors.^{31–33} In general,
white light can be generated by the simultaneous emission of

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73 blue, green, and red colors or of two complementary colors
 74 (e.g., blue and orange), including the entire visible spectrum.
 75 Obtaining soft materials able to emit white light that can be
 76 easily handled in the solid form is a challenge, and there are
 77 only a few examples in literature.^{34,35} Consequently, obtaining
 78 such materials poses a challenge for the scientific community.
 79 We report here the synthesis of a physical phenyl-
 80 diaminotriazine (PhDAT) hydrogel by radical polymerization
 81 of acrylic and vinyl monomers: acrylamide (AM), oligo-
 82 (ethylene glycol) methyl ether methacrylate (OEGMA) and 6-
 83 (4-vinylphenyl)-2,4-diamino-1,3,5-triazine (VPhDT; **Scheme**
 84 **1**).³⁶ VPhDT is a multifunctional monomer because it can take

Scheme 1. Synthesis and Proposed Structure of the PhDAT Hydrogel



85 part in numerous noncovalent interactions: metal coordina-
 86 tion, acceptor and donor H-bond, π - π stacking, π -cation, and
 87 π - σ and lone-pair interactions.^{37,38} Monomers such as AM
 88 and OEGMA act as hydrophilic counterparts in order to offset
 89 the intrinsic hydrophobicity of VPhDT, thus, allowing the
 90 hydrogel to swell in water.³⁹

91 The VPhDT monomer was prepared by a modified version
 92 of a previously described method (see SI, S1–S4).⁴⁰ X-ray
 93 diffraction (Figures S5–S7) on this compound showed an
 94 interesting supramolecular structure with two linear chains
 95 assembled by CH- π and NH-N hydrogen-bonding inter-
 96 actions. However, this crystalline structure did not show any
 97 fluorescence properties.

98 The hydrogel was prepared by radical polymerization of
 99 monomers in DMSO using potassium persulfate (KPS) as the
 100 radical initiator. The reaction was carried out at 90 °C for 30
 101 min in a preheated silicone cylindrical mold (see SI). When the
 102 polymerization was complete, the organogel was removed from
 103 the mold, followed by washing with distilled water for 3 days.

104 During the washings, DMSO was phase-inverted with water
 105 and leached out of the hydrogel, along with unreacted
 106 monomers. The tentative structure of PhDAT is shown in
 107 **Scheme 1**. Fourier transform infrared (FTIR) spectroscopy
 108 was used to confirm the formation of the copolymer chains
 109 network constituting the PhDAT hydrogel (**Figure S8**). The
 110 mechanical properties of the hydrogel were tested. The
 111 compressive Young's modulus (E) and the absorbed energy
 112 of the PhDAT hydrogels were 21.76 ± 1.23 kPa (calculated
 113 between 2% and 10% of strain) and 0.70 ± 0.06 (determined
 114 to be 0–15% area under the stress-strain curve), respectively
 115 (**Figure S9**).

116 Despite the fact that a covalent cross-linker was not used, a
 117 robust hydrogel was obtained (inset **Figure 1**). Hydrogen

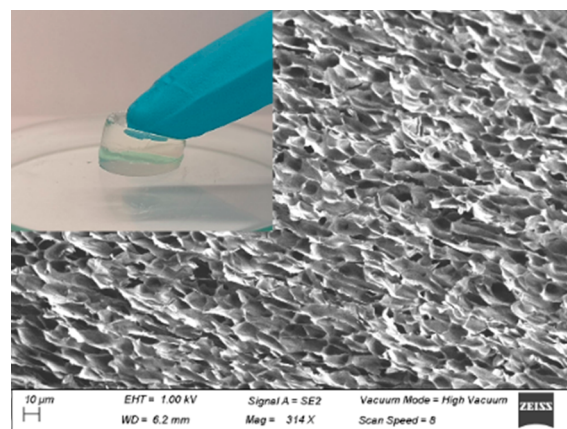


Figure 1. SEM image of the hydrogel at pH 7.4 (inset: digital image of the hydrogel).

118 bonds and hydrophobic interactions are responsible for
 119 maintaining the 3D structure.^{41,42} A scanning electron
 120 microscopy (SEM) image of the physical hydrogel confirmed
 121 its typical porous morphology (**Figure 1**). The hydrogel can
 122 swell in aqueous media, thus, demonstrating its absorption
 123 ability. The swelling ratio at different pH values was studied by
 124 gravimetric analysis (**Figure S10**).

125 The monomers themselves did not show any light response
 126 when irradiated under UV light, either in solution or in the
 127 solid state. An explanation of why VPhDT does not show AIE
 128 behavior in solution could be related with the free movement
 129 of monomers, which leads to mechanisms of motion-induced
 130 quenching of fluorescence. In solid state, the absence of
 131 fluorescence must be related to the stacking observed in the
 132 X-ray diffraction analysis. However, the hydrogel had blue
 133 fluorescence (466–468 nm) when irradiated at 373 nm
 134 (**Figure 2**). On this basis, we propose that the AIE behavior
 135 arises from the incorporation of the phenyltriazine derivative
 136 into the 3D polymeric network. In the PhDAT-based hydrogel,
 137 where the diaminotriazine moieties are tightly immobilized
 138 through intermolecular hydrogen bonds, the energy is emitted
 139 as fluorescence, since intramolecular motions are restricted.
 140 Moreover, the randomized distribution of the triazine moieties
 141 in the network prevents the stacking observed in the solid
 142 state. It is important to note that the same hydrogel prepared
 143 without the VPhDT monomer does not present fluorescence.

144 The situation described above is reflected in the fluorescence
 145 intensity values with respect to the swelling state of the
 146 hydrogel (**Figure 2**). It can be seen that higher intensity values
 147 were recorded for the hydrogel in its dried state (i.e., xerogel).

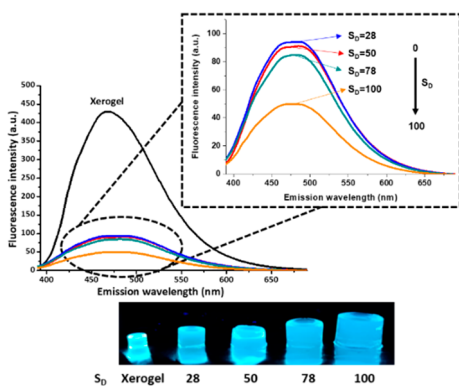


Figure 2. Dependence of fluorescent behavior on swelling degree (S_D) at $\lambda_{\text{exc}} = 373$ nm and digital images of fluorescent PhDAT hydrogels under UV light ($\lambda_{\text{exc}} = 365$ nm).

148 Phenyltriazine moieties in this state are in their closest
149 proximity and they, therefore, experience the highest AIE
150 fluorescence. As the water content within the polymer network
151 increases, the pores expand and the phenyltriazine domains
152 move further away from each other, which leads to a notable
153 decrease in the fluorescence (Figure 2, inset).

154 Surprisingly, the hydrogel still showed AIE in its maximum
155 swollen state. This remarkable result can be explained by the
156 strong hydrogen-bonding interactions between triazine moi-
157 eties: although forced to expand in the presence of water,
158 triazine molecules still remain close to one another due to the
159 formation of strong hydrogen-bonding pairs, which arrange
160 into hydrophobic microdomains, as reported previously for
161 diaminotriazine skeletons.^{39,43} These domains not only restrict
162 molecular motions (RIM), but also bring together neighboring
163 triazine molecules, both of which maintain fluorescence and
164 enhance the AIE effect, despite the fact that the hydrogel is not
165 in its maximum dry state.

166 Further evidence for this mechanism was provided by
167 measuring the fluorescence while changing the pH of the
168 medium. It can be seen from Figure 3 that the PL values drop

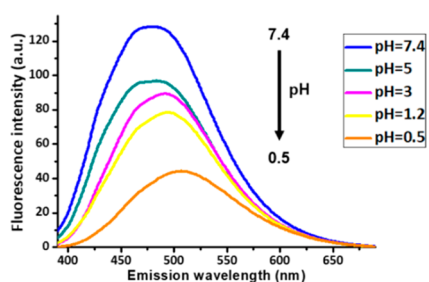


Figure 3. Fluorescence spectra of PhDAT hydrogel under UV light ($\lambda_{\text{exc}} = 373$ nm) at the initial swelling stage in different pH media.

169 dramatically on decreasing the pH. These experiments were
170 carried out on samples in the initial swelling states ($SD = 28$)
171 with the appropriate buffered solution. It is remarkable that the
172 hydrogel maintains a high PL intensity, even at $pH = 1.2$, with
173 more extreme acid conditions required to decrease significantly
174 the PL intensity. This fact must be related to the low basicity of
175 the triazine ring.⁴⁴

176 Indeed, in acidic media, the triazine molecules are
177 protonated and repel each other due to electrostatic repulsion;
178 consequently, the hydrogels reach their maximum swelling

degree at $pH = 0.5$ ($SW = 25 \pm 0.56$). The protonation of the
179 triazine ring provides two significant effects: the partial rupture
180 of the hydrogen bond network⁴⁵ and the modification of the π
181 system. The former must be related to the decrease of the
182 fluorescence intensity due to the increased mobility of the
183 chromophores (Figure 4). The latter is consistent with the
184 bathochromic shift caused by the increased electro-
185 negativity of the triazine ring.⁴⁶ 186

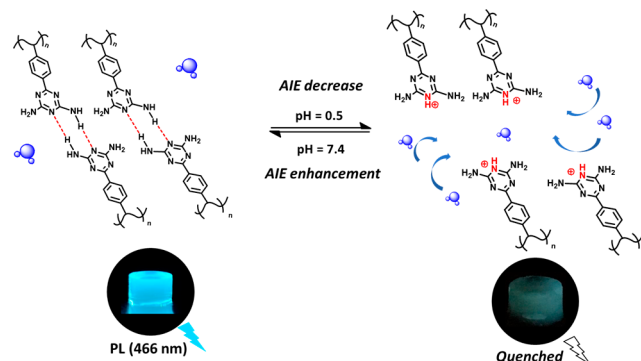


Figure 4. Schematic illustration of pH-responsiveness and proposed AIE mechanism for PhDAT swollen hydrogels.

In order to test the reversibility of the process, cycling
187 experiments were carried out between $pH = 7.4$ and $pH = 0.5$. The
188 fluorescence intensity of the hydrogel decreased as the pH
189 decreased from 7.4 to 0.5, whereas it was restored when the
190 pH was readjusted to 7.4 (Figure S11). 191

Taking advantage of the inherent blue emission of the
192 hydrogel, we added two chromophores inside the gel in order
193 to obtain a white-light-emitting material. For this purpose,
194 fluorescein and rhodamine 101 are incorporated into the gel in
195 appropriate proportions, as green and red fluorophores,
196 respectively. Upon irradiation at 386 nm and following a
197 Förster Resonance Energy Transfer, a white light of (0.27, 0.36)
198 CIE coordinates⁴⁷ was observed (Figure 5, see SI). 199

In conclusion, a novel phenyldiaminotriazine-based hydrogel
200 has been developed. This polymeric 3D network has a soft
201 scaffold structure with aggregation-induced emission. In
202 contrast to supramolecular gels, this hydrogel can be easily
203 handled in the solid form. The anchoring of phenyltriazine 204

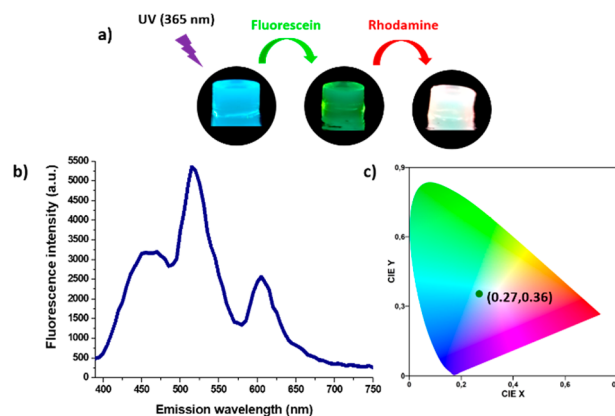


Figure 5. (a) Luminescent emission of the PhDAT hydrogel under UV light after incorporation of fluorescent dyes. (b) Fluorescence spectrum and (c) CIE (x,y) chromaticity diagram of the white-light-emitting hydrogel.

205 groups in the polymer chains leads to the formation of
206 microdomains due to aggregation of triazine moieties by
207 hydrogen bonding. The topology of the network restricts the
208 movement of fluorophores (RIM), which results in a
209 fluorescent emission by AIE. Remarkably, the polymer network
210 can absorb water while maintaining the 3D integrity and the
211 fluorescent behavior. The fluorescence of the hydrogel is only
212 diminished in strongly acidic media. Therefore, this new blue-
213 light-emitting material could be used as a sensor for ions or
214 molecules capable of interacting with the different functional
215 groups of the polymer network in a reversible way without
216 losing the chromophore. In addition, the possibility of adding
217 other fluorophores to the hydrogel allows obtaining a new soft
218 material that emits white light.

219 ■ ASSOCIATED CONTENT

220 ● Supporting Information

221 The Supporting Information is available free of charge on the
222 ACS Publications website at DOI: [10.1021/acsmacro-](https://doi.org/10.1021/acsmacrolett.9b00712)
223 [lett.9b00712](https://doi.org/10.1021/acsmacrolett.9b00712).

224 Synthesis and characterization of VPhDT, including X-
225 ray diffraction data, preparation conditions, mechanical
226 properties, and influence of pH variation of the hydrogel
227 (PhDAT); experiments on hydrogel light emission
228 (PDF)

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238 Author Contributions

239 The manuscript was written through contributions of all
240 authors. All authors have given approval to the final version of
241 the manuscript.

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244 Notes

245 The authors declare no competing financial interest.

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