# Supporting Information

# Photoconverting waste amphiphiles at the mild air-water interface into easily separable value-added products

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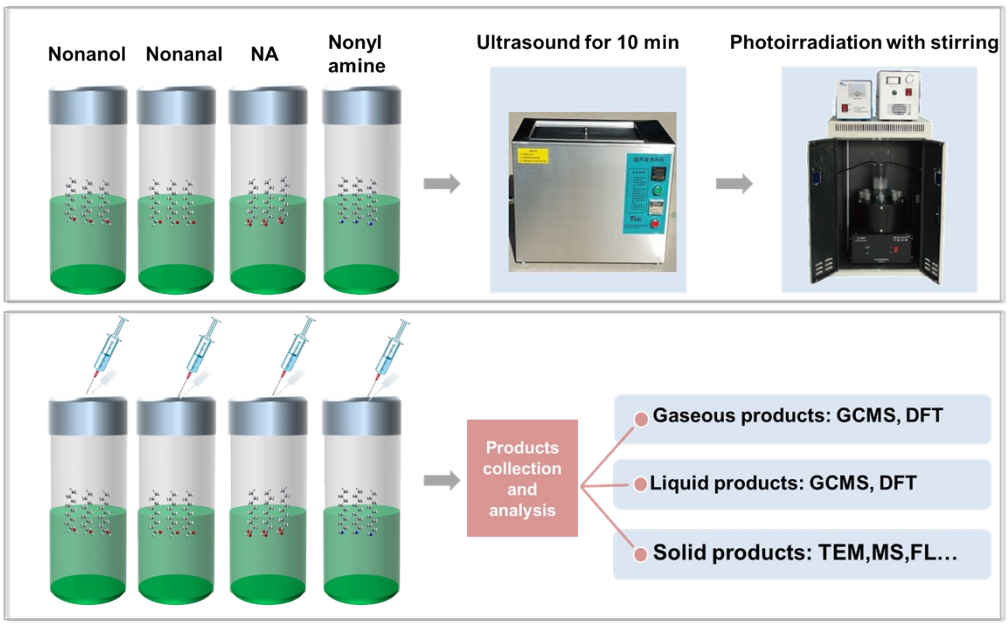


**Fig. S1** Schematic diagram of converting 4 types of waste surfactants into value-added products and their collection and analysis.

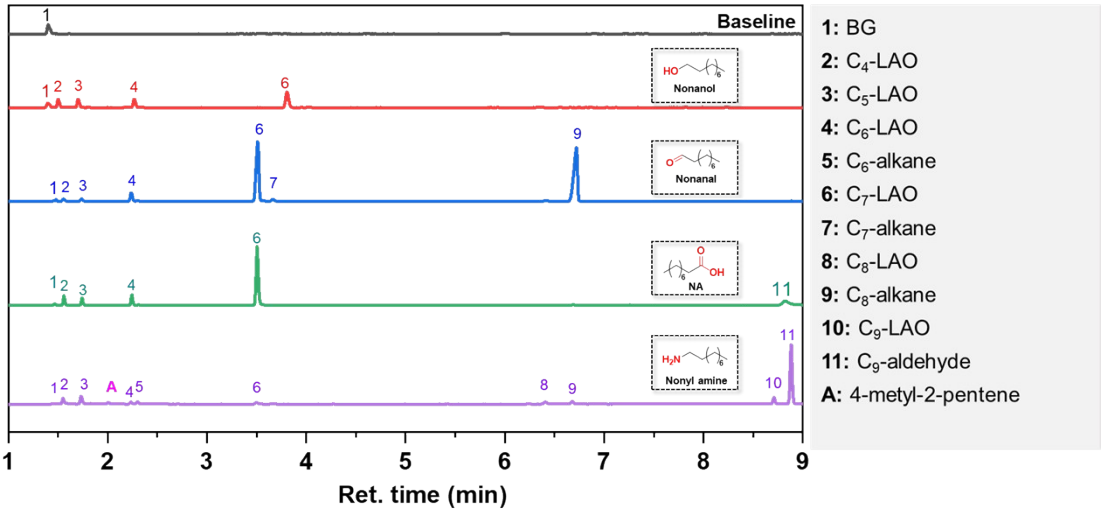


**Fig. S2** GC-MS spectra from different waste surfactants under interfacial photochemistry.

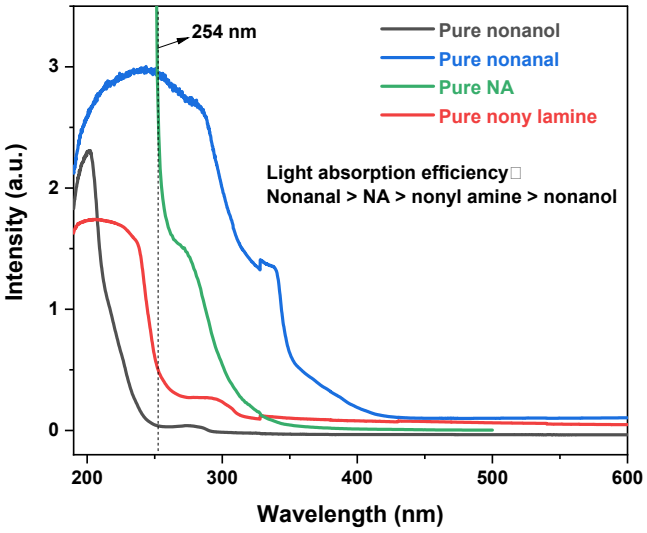


**Fig. S3** UV-vis spectra of different pure surfactants.

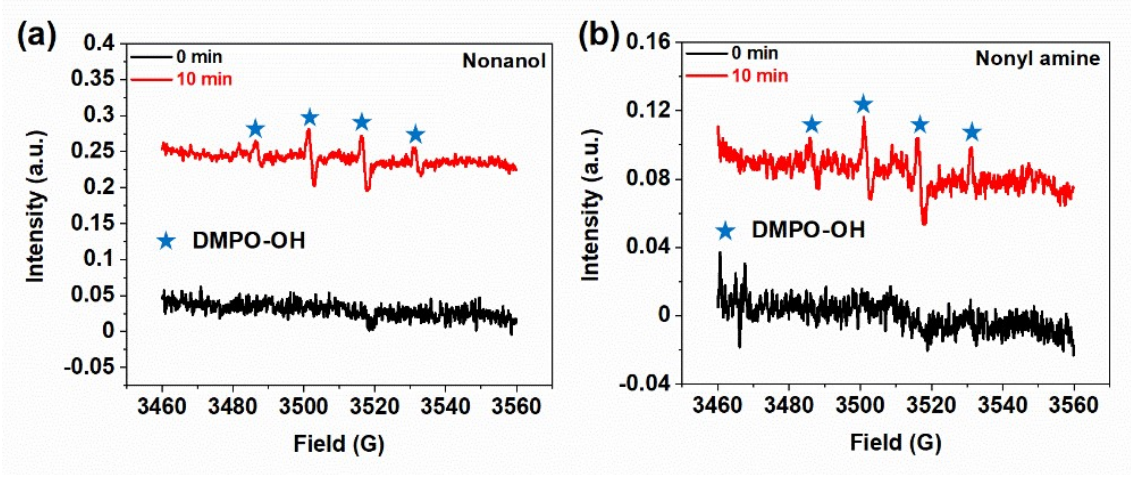


**Fig. S4** ESR spectra of DMPO-OH obtained from (a) nonanol and (b) nonyl amine under interfacial photoirradiation.

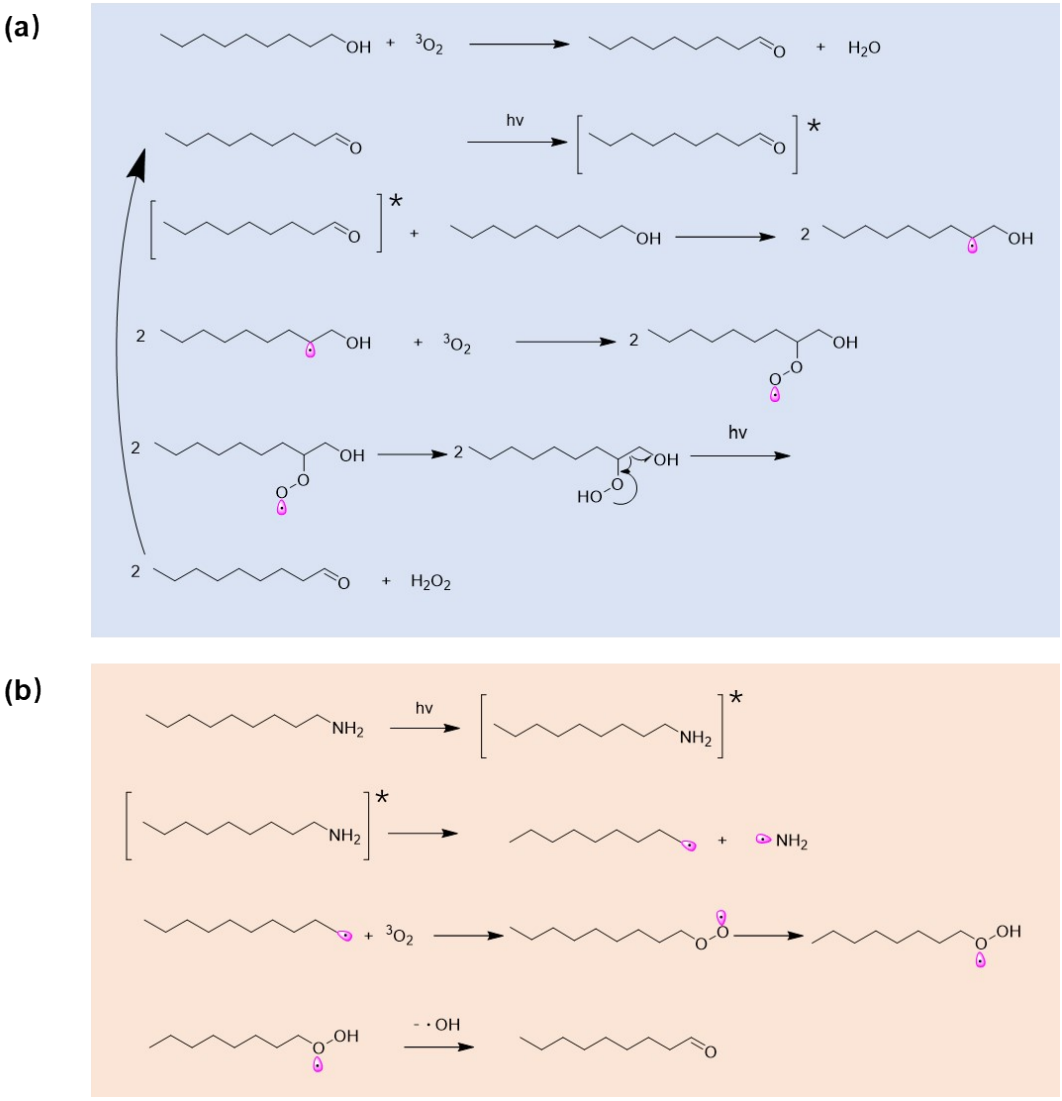


**Fig. S5** The mechanism and pathway of the formation of nonanal from (a) nonanol and (b) nonyl amine under interfacial photoirradiation.

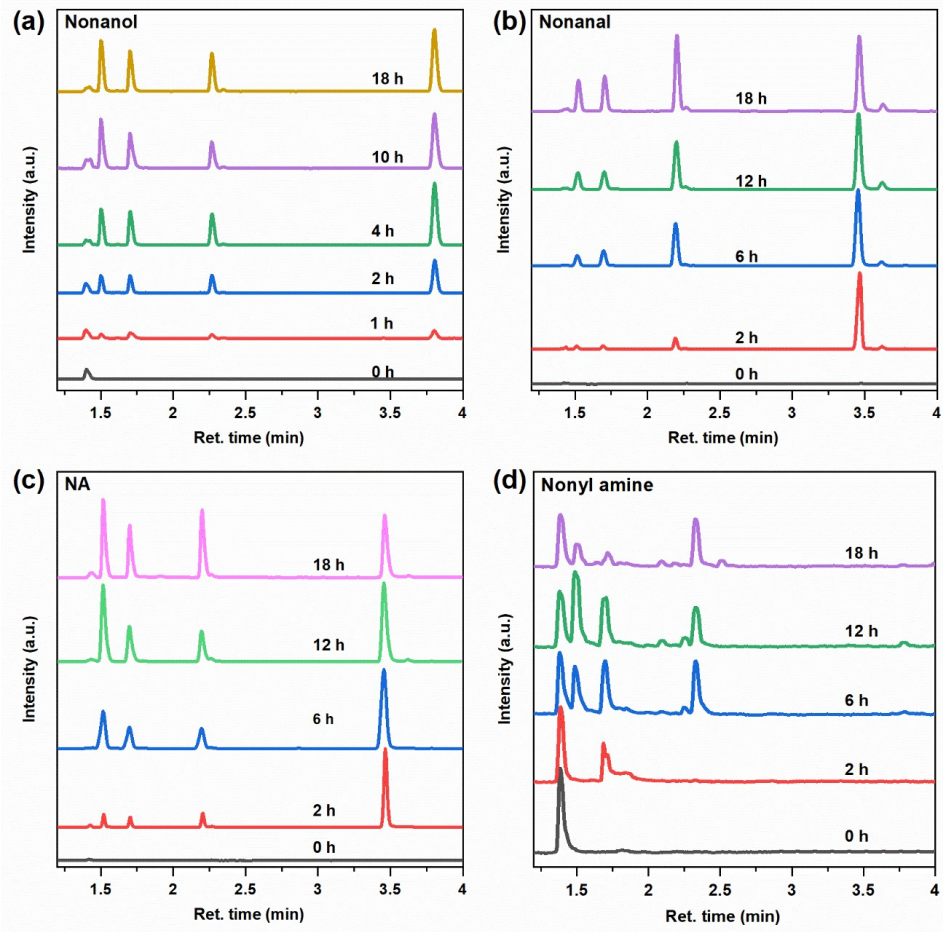


**Fig. S6** The peaks of gaseous products from different surfactants upon different photoirradiation time: (a) nonanol; (b) nonanal; (c) NA; (d) nonyl amine.

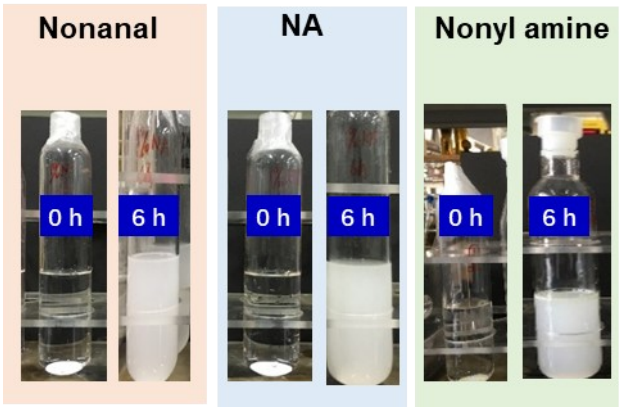


**Fig. S7** Nonanal, NA and nonyl amine solutions before (0 h) and after photoirradiation (6 h)

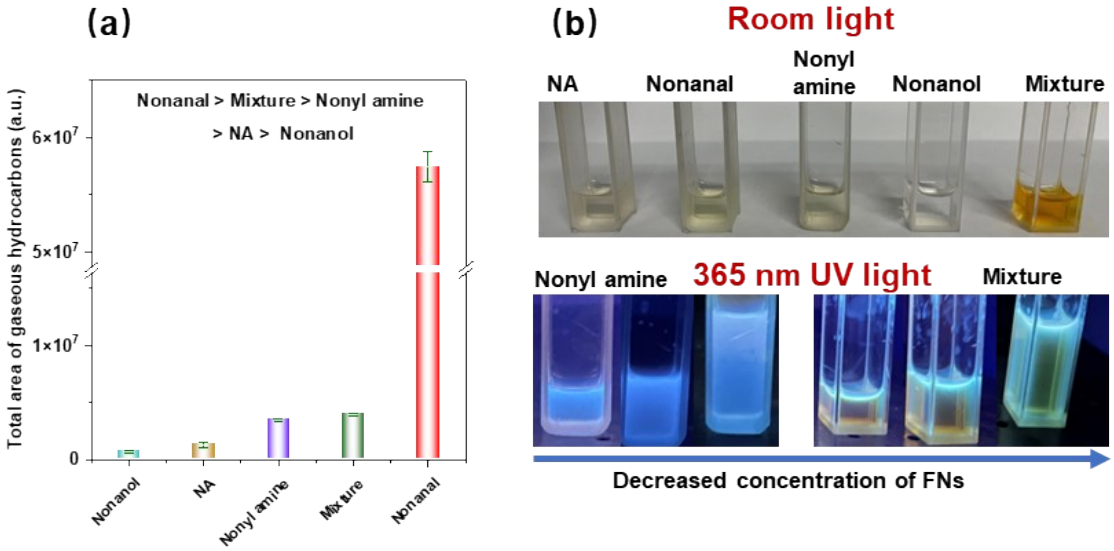


**Fig. S8** (a) Comparison of total gas production (/mM) and (b) solid FNs-containing solutions obtained from mixed system and individual system after interfacial photoirradiation.

Surprisingly, **Fig.S8b** that the conversion tendency of solid fluorescent nanoparticles (FNs) in the mixed system is strengthened. This is because the darker yellow color of mixed system under room light compared to the individual system indicating its high concentration of FNs. Under 365-nm UV light, the FNs-containing solution from mixed system displayed a significant fluorescence quenching effect, while the FNs-containing from nonyl amine alone did not, further supporting the production of higher concentrations of FNs in the mixed system.[1] The above results indicate that mixing different types of surfactants together can synergistically significantly enhance their conversion to solid-phase FNs. The mechanism of synergistic enhancement for FNs production in the mixed system would be investigated in the future.

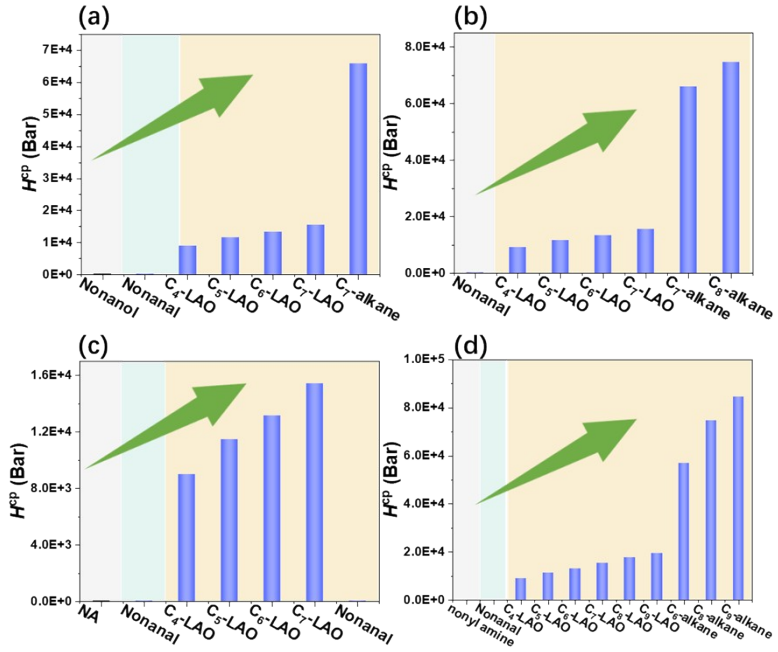


**Fig. S9** Comparison of the Henry's constant of gaseous products with their precursors.

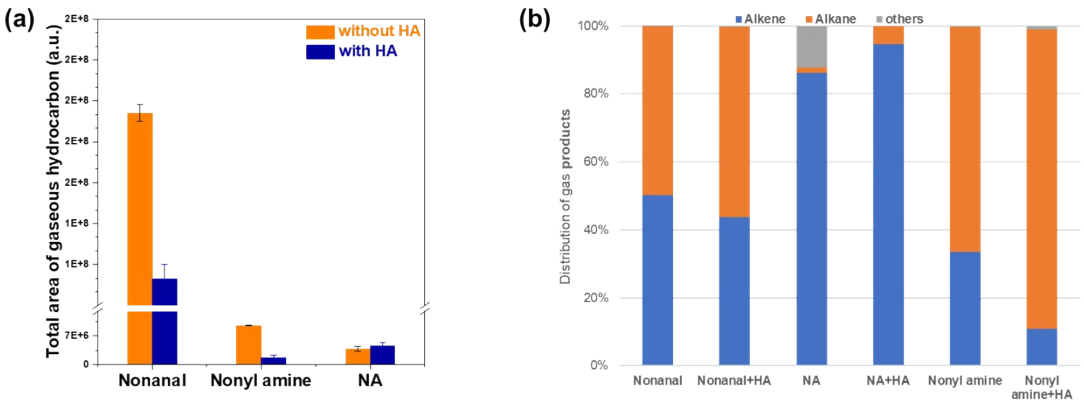


**Fig. S10** Effect of humic acid on the (a) yield and (b) distribution and of gas products.

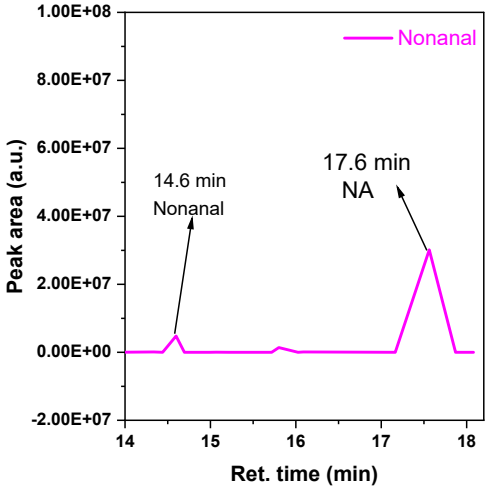


**Fig. S11** The conversion of nonanal to NA upon photoirradiation for 5h.

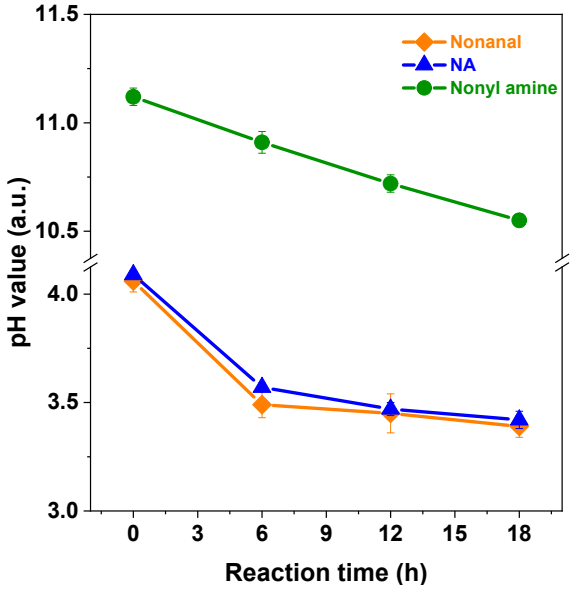


**Fig. S12** Changes of pH value of different surfactant system with respect to time.

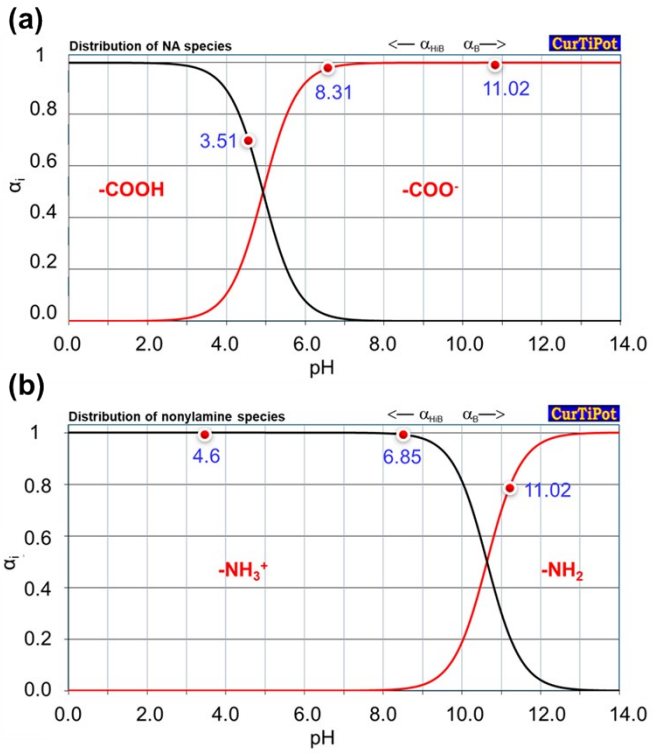


**Fig. S13** The morphological distribution of NA (a) and Nonyl amine (b) at different pH.

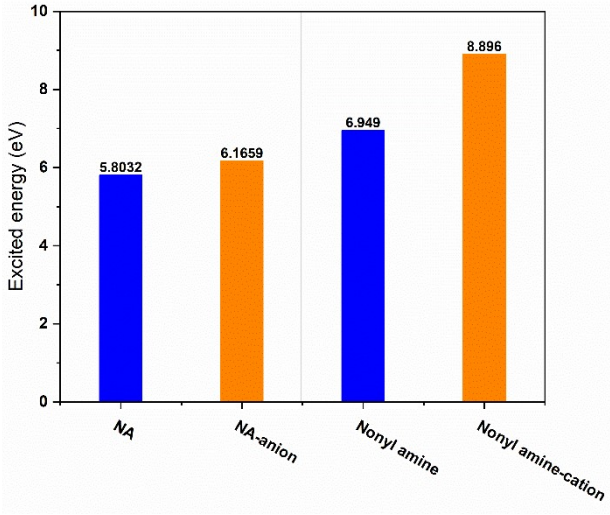


**Fig. S14** Comparison of first vertical exited energies between neutral NA and NA anion, neutral nonyl amine and nonyl amine cation.

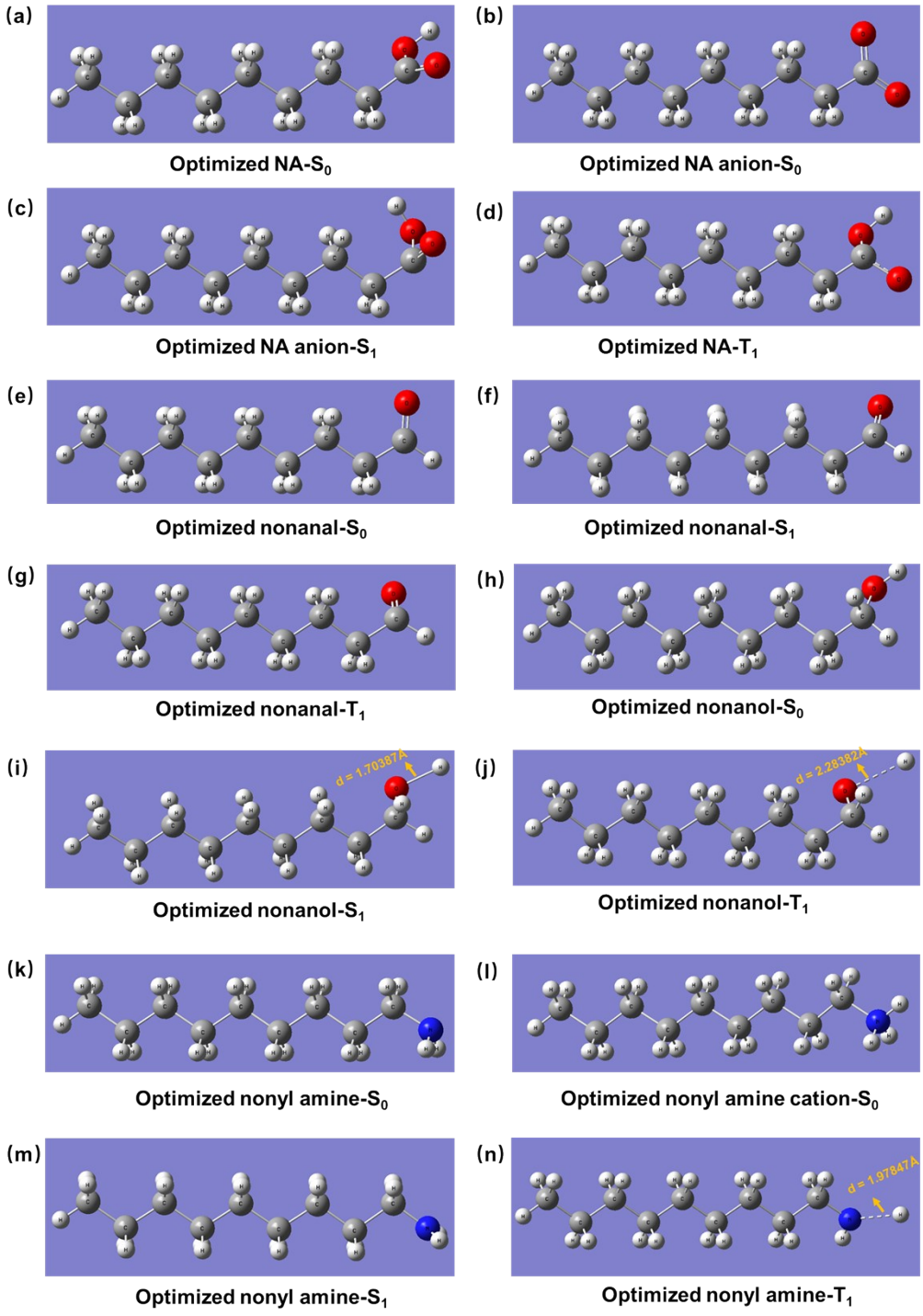


**Fig. S15** Optimized ground state ($S_0$), singlet ($S_1$) and triplet ($T_1$) structures of various surfactants.

**Table S1** Energies for reactants and products calculated at M062X/def2TZVP level.

| Name | Zero-point energy (hatree) | Thermal correction to Enthalpy (hartree) | Thermal correction to Gibbs free energy (hartree) | Single point energy (hartree) | H (298.15K, hartree) | G (298.15K, hartree) |
|---|---|---|---|---|---|---|
| Nonanol ($S_0$) | 0.280638 | 0.295045 | 0.239513 | -430.182754 | -429.887709 | -429.943241 |
| Nonanol ($S_1$) | 0.269277 | 0.284155 | 0.227332 | -429.963023 | -429.887709 | -429.735691 |
| Nonanol ($T_1$) | 0.266077 | 0.280196 | 0.225591 | -430.00267 | -429.887709 | -429.777079 |
| $CH_3(CH_2)_7$-·COH | 0.266953 | 0.281384 | 0.225162 | -429.524335 | -429.242951 | -429.299173 |
| $CH_3(CH_2)_7$-C(OO·)OH | 0.277044 | 0.293248 | 0.231639 | -579.918691 | -579.625443 | -579.687052 |
| $CH_3(CH_2)_7$-C(OOH)OH | 0.289036 | 0.305706 | 0.24392 | -580.56324 | -580.257534 | -580.31932 |
| Nonanal ($S_0$) | 0.256452 | 0.270324 | 0.215694 | -428.977769 | -428.707445 | -428.762075 |
| Nonanal ($S_1$) | 0.253182 | 0.267389 | 0.212106 | -428.835733 | -428.568344 | -428.623627 |
| Nonanal ($T_1$) | 0.25303 | 0.267217 | 0.210734 | -428.85002 | -428.582803 | -428.639286 |
| NA ($S_0$) | 0.262612 | 0.277378 | 0.218827 | -504.245779 | -503.968401 | -504.026952 |
| NA ($S_1$) | 0.258403 | 0.273829 | 0.215125 | -504.060099 | -503.78627 | -503.844974 |
| NA ($T_1$) | 0.258782 | 0.274113 | 0.214761 | -504.0826 | -503.808487 | -503.867839 |
| NA anion ($S_0$) | 0.249106 | 0.263617 | 0.206018 | -503.776594 | -503.512977 | -503.570576 |
| Nonyl amine ($S_0$) | 0.293253 | 0.307892 | 0.251743 | -410.307906 | -410.000014 | -410.056163 |
| Nonyl amine ($S_1$) | 0.282658 | 0.297638 | 0.241057 | -410.084388 | -409.78675 | -409.843331 |
| Nonyl amine ($T_1$) | 0.279758 | 0.293952 | 0.239215 | -410.133702 | -409.83975 | -409.894487 |
| Nonyl amine cation ($S_0$) | 0.309069 | 0.323717 | 0.267645 | -410.760895 | -410.437178 | -410.49325 |
| $CH_3(CH_2)_6$-$CH_2$-•$CH_2$ | 0.2601 | 0.274048 | 0.218958 | -354.28542 | -354.011372 | -354.066462 |
| •$NH_2$ | 0.019203 | 0.022984 | 0.000244 | -55.874531 | -55.851547 | -55.874287 |
| $CH_3(CH_2)_6$-•CH-•$CH_2$ | 0.245981 | 0.25983 | 0.204966 | -353.620117 | -353.360287 | -353.415151 |
| $CH_3(CH_2)_6$-•$CH_2$ | 0.231571 | 0.244143 | 0.192813 | -314.978184 | -314.734041 | -314.785371 |
| •$CH_2NH_2$ | 0.050184 | 0.054584 | 0.02702 | -95.191524 | -95.13694 | -95.164504 |
| $^3O_2$ | 0.004023 | 0.007329 | -0.015914 | -150.32731 | -150.319981 | -150.343224 |
| $^1O_2$ | 0.004011 | 0.007317 | -0.014886 | -150.268976 | -150.261659 | -150.283862 |
| $H_2O$ | 0.021392 | 0.025172 | 0.003748 | -76.433708 | -76.408536 | -76.42996 |
| $H_2O_2$ | 0.027054 | 0.031192 | 0.005469 | -151.559208 | -151.528016 | -151.553739 |
| H• | 0 | 0.00236 | -0.010654 | -0.498162 | -0.495802 | -0.508816 |

**Table S2** Calculated reaction energies at M062X/def2TZVP level.

| Chemical reaction | ΔG (kJ/mol) or cleavage energy |
|---|---|
| $2CH_3(CH_2)_8OH + {}^3O_2 = 2\,{}^3CH_3(CH_2)_7\text{-}C(H)=O + 2H_2O$ | -561.137613 |
| ${}^3CH_3(CH_2)_7\text{-}C(H)=O + CH_3(CH_2)_7\text{-}COH = 2CH_3(CH_2)_7\text{-}\bullet COH$ | -41.5327845 |
| $2CH_3(CH_2)_7\text{-}\bullet COH + O2 = 2CH_3(CH_2)_7\text{-}C(OO\bullet)OH$ | -117.2417025 |
| $2CH_3(CH_2)_7\text{-}C(OOH)OH = H_2O_2 + CH_3(CH_2)_7\text{-}C(H)=O$ | 9.205003 |
| $CH_3(CH_2)_8\text{-}NH_2 = \bullet NH_2 + CH_3(CH_2)_7\text{-}CH_2\bullet$ | 303.0195 |
| $CH_3(CH_2)_8\text{-}NH_2 = \bullet CH_2NH_2 + CH_3(CH_2)_6\text{-}CH_2\bullet$ | 279.059144 |
| $CH_3(CH_2)_7\text{-}CH_2\bullet = \bullet H + CH_3(CH_2)_6\text{-}\bullet CH\text{-}CH_2\bullet$ | 374.0523595 |

**Table S3** Cost estimation for the process of converting 1 ton of NA wastewater into high value-added products

| Methods | NA concentration in water (mM) | Product parameter ($C_7$-LAO) | Key reagent and unit price | Reagent cost ($/m$^3$) | Energy cost ($/m$^3$) | Operating cost ($/m$^3$) | Ref. |
|---|---|---|---|---|---|---|---|
| Chemical heterogeneous catalysis | 0.05-2[2-4] | Selectivity: 45-80%<br>Conversion rate: 0.7-11.1% | Catalyst: Pt/C (40-45 $/g)<br>Norit activated carbon (450 $/ton)<br>$N_2$ (4.7-4.8 $/m$^3$) | 115.7-214.3 | 1028.5-1285.7 | 1144.3-1500 | [5] |
| Chemical homogeneous catalysis | 0.05-2[2-4] | Selectivity: 84-91%<br>Conversion rate: 59-78% | Catalyst: Pt (40-45 $/g)<br>γ-valerolactone (3805-3880) $/ton | 1628.6-1691.4 | 30-40 | 1658.6-1731.5 | [6] |
| Enzymatic catalysis | 0.05-2[2-4] | Product yield: 40-70% | NADPH: 21500 $/mol | >9890 | | >9890 | [7, 8] |
| Gas-water interfacial photoirradiation | 0.05-2[2-4] | Selectivity: 87%-91%<br>Conversion rate: 60-99% | | | 800-511.14 | 800-511.14 | Our work |

Note: energy cost was calculated based on the electricity (0.1085$/kWh)[9] and reagent cost was calculated based on the market price and literatures.

**Notes and references**

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