

Electronic Supplementary Information (ESI) for

Revealing the sensing mechanism of a fluorescent pH probe based on a bichromophore approach

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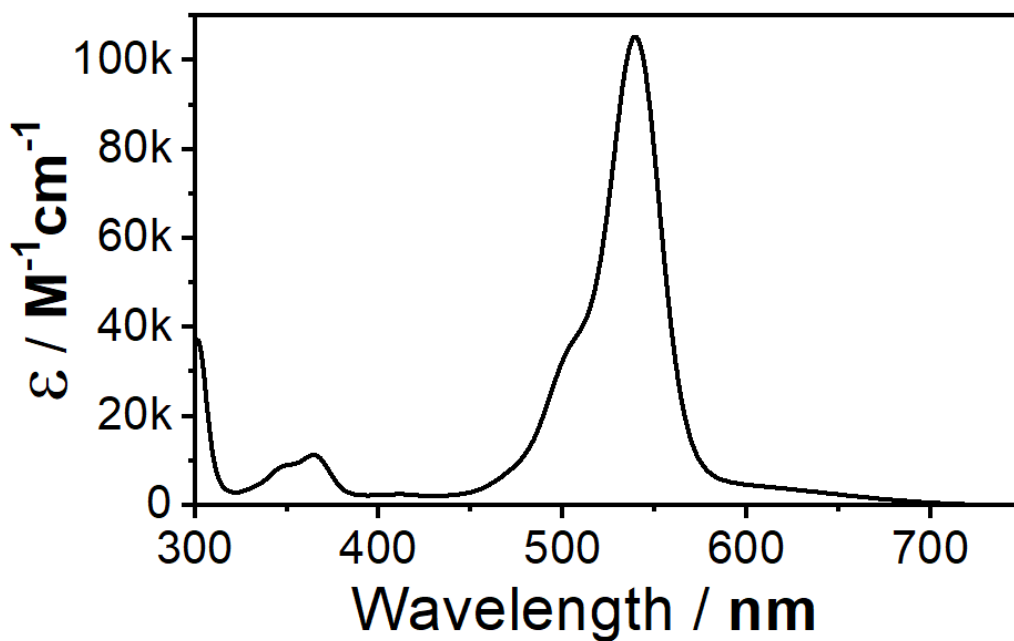


Fig. S1 Molar absorption coefficient of TMARh in acetonitrile.

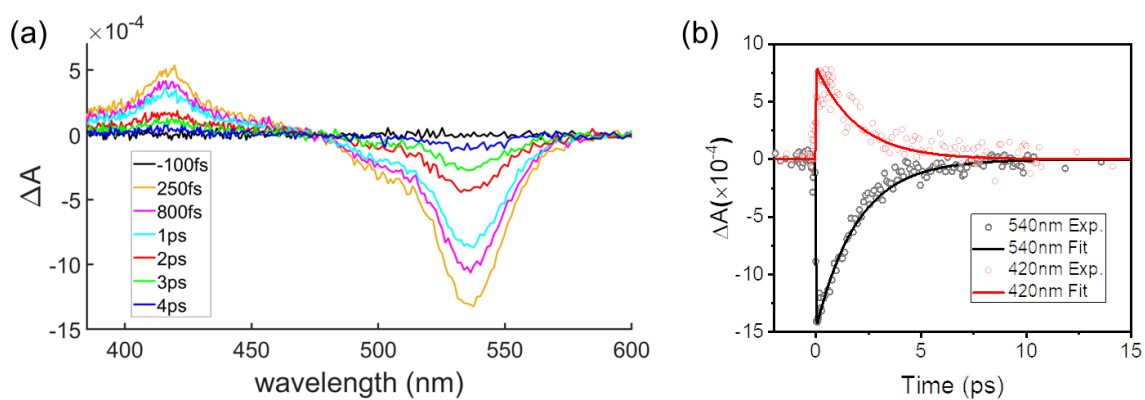


Fig. S2 (a) fs-TA spectra of TMARh with excitation at 630nm, (b) the kinetic traces at 540 nm and 420 nm. Fitted decay time $\tau=1.8\pm 0.3$ ps.

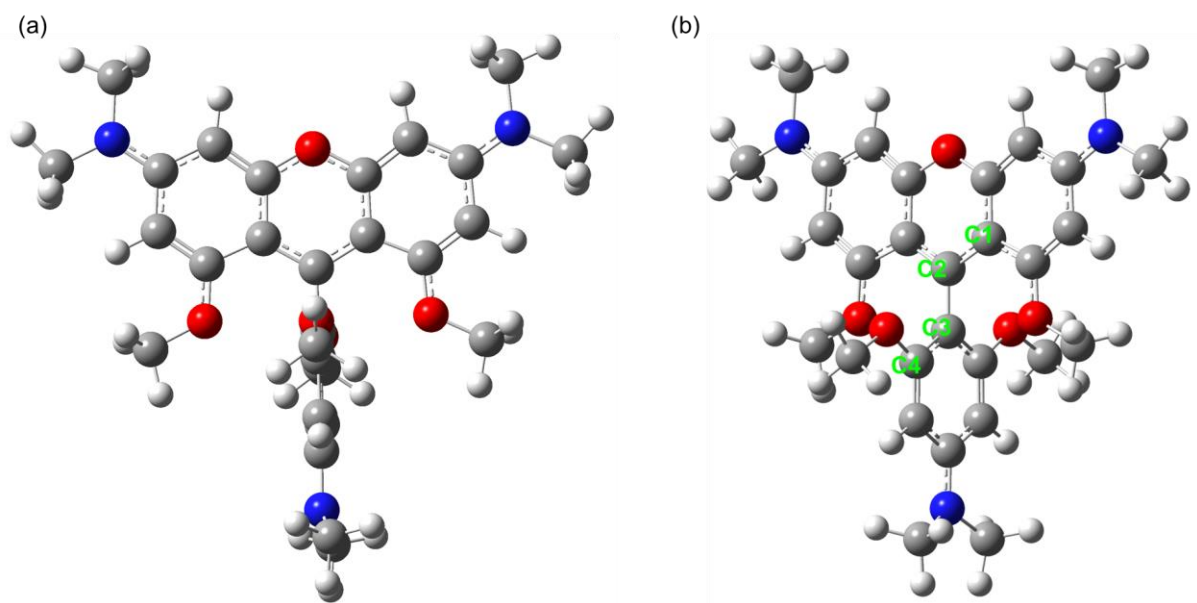


Fig. S3 Optimized geometry of TMARh in S_0 state (a) front view and (b) side view with dihedral angle ($C1-C2-C3-C4=91.7^\circ$) between the xanthenium and phenyl groups.

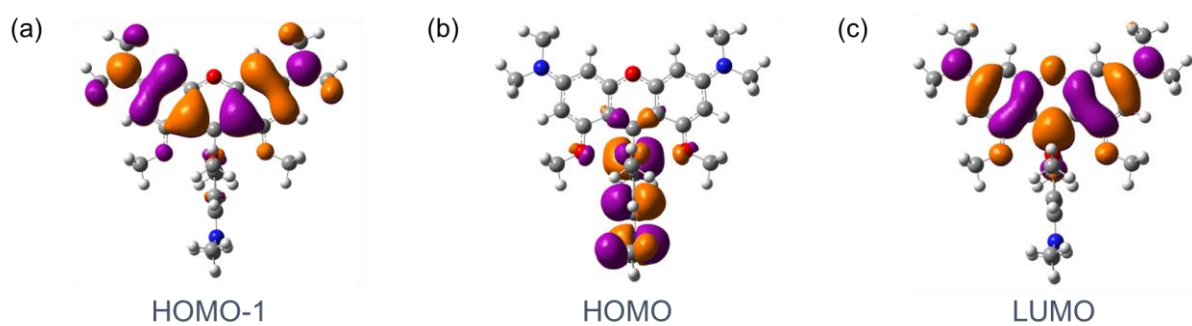


Fig. S4 (a) HOMO-1, (b) HOMO and (c) LUMO of TMARh based on the optimized S_0 state geometry.

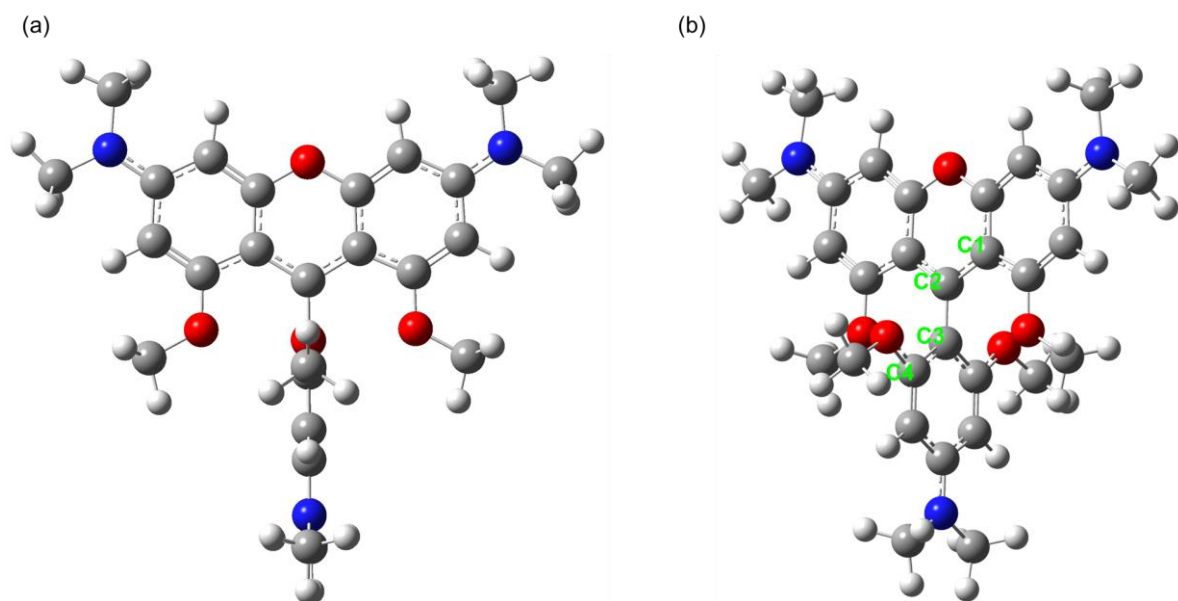


Fig. S5 Optimized geometry of TMARh in S_1 state (a) front view and (b) side view with dihedral angle ($C1-C2-C3-C4=90.1^\circ$) between the xanthenium and phenyl groups.

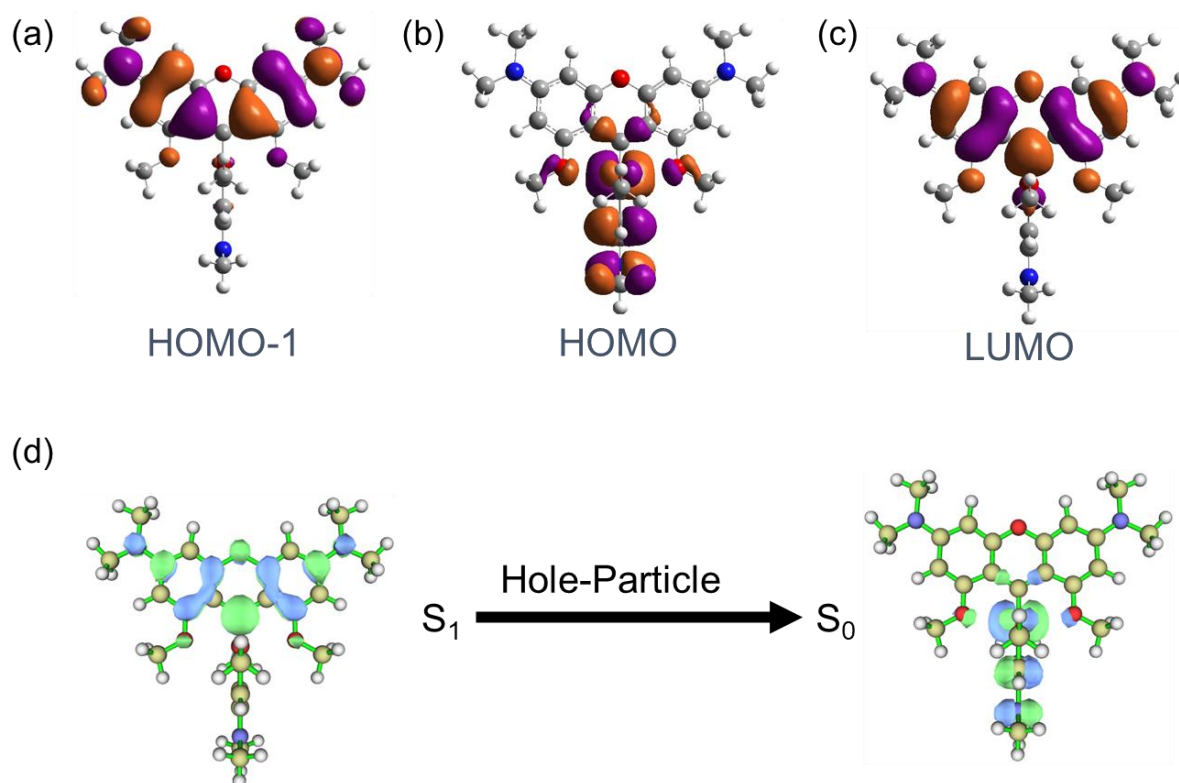


Fig. S6 (a) HOMO-1, (b) HOMO, (c) LUMO and the nature transition orbital analyzes of TMARh based on the optimized S_1 state geometry.

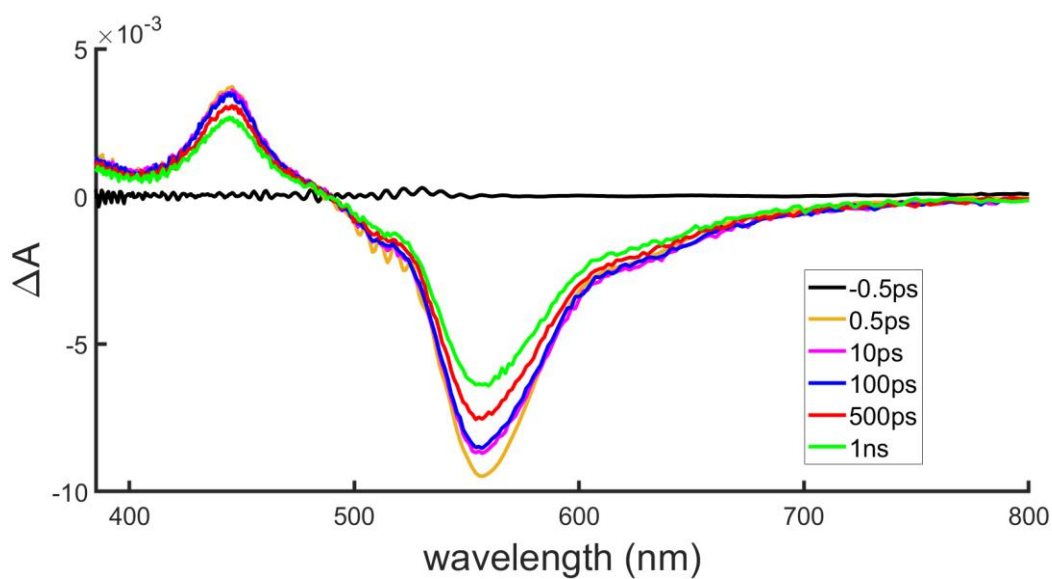


Fig. S7 fs-TA spectra of HTMARh with excitation at 530nm.

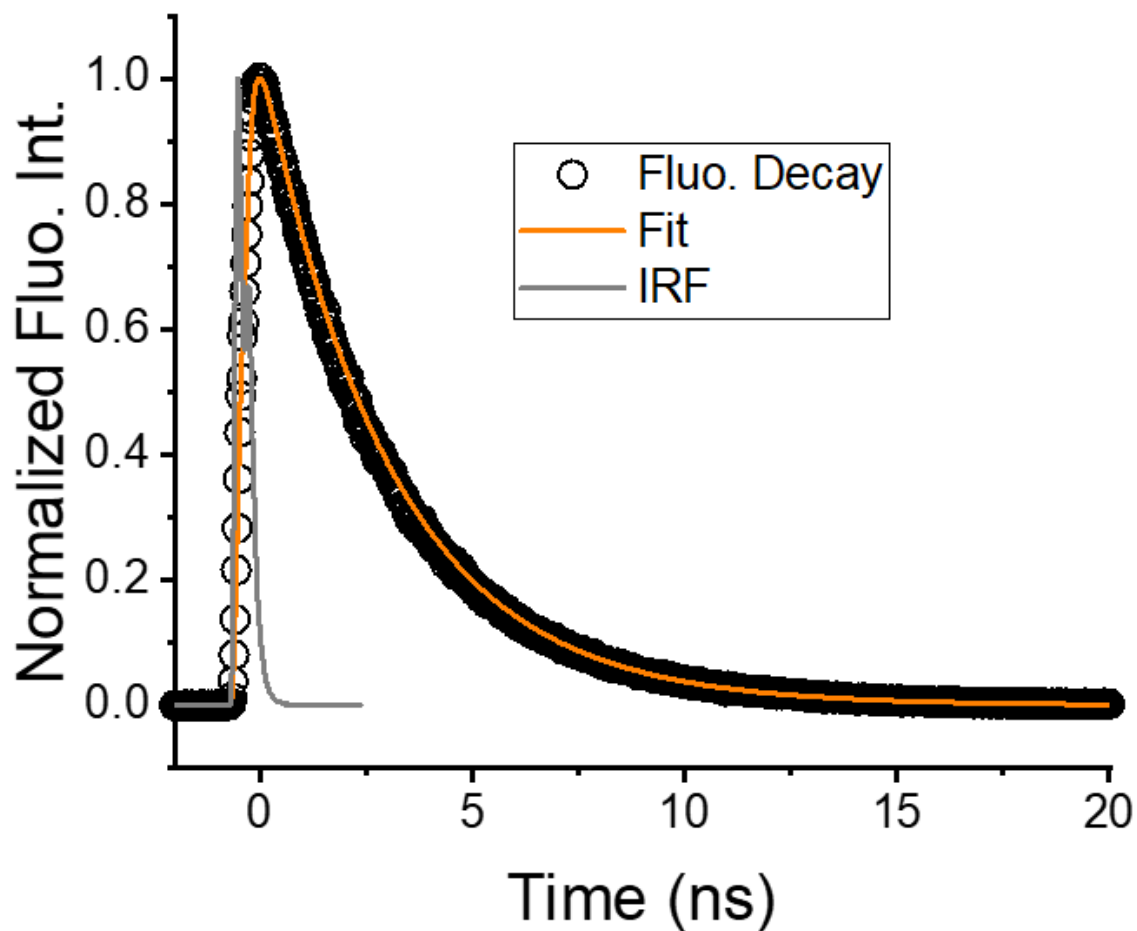


Fig. S8 Normalized fluorescence intensity decay of HTMARh with excitation at 530 nm and detection at 580 nm, IRF: instrument response function. The mono-exponential fit gives the fluorescence decay lifetime of 3.0 ± 0.2 ns.

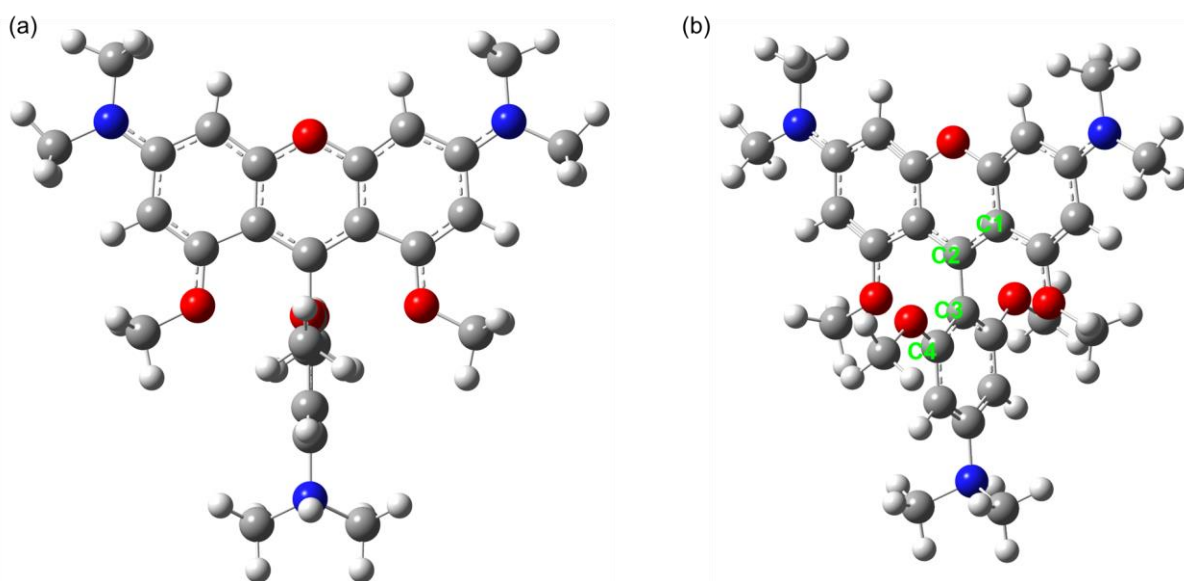


Fig. S9 Optimized geometry of HTMARh in S_0 state (a) front view and (b) side view with dihedral angle ($C1-C2-C3-C4=88.5^\circ$) between xanthenium and phenyl groups.

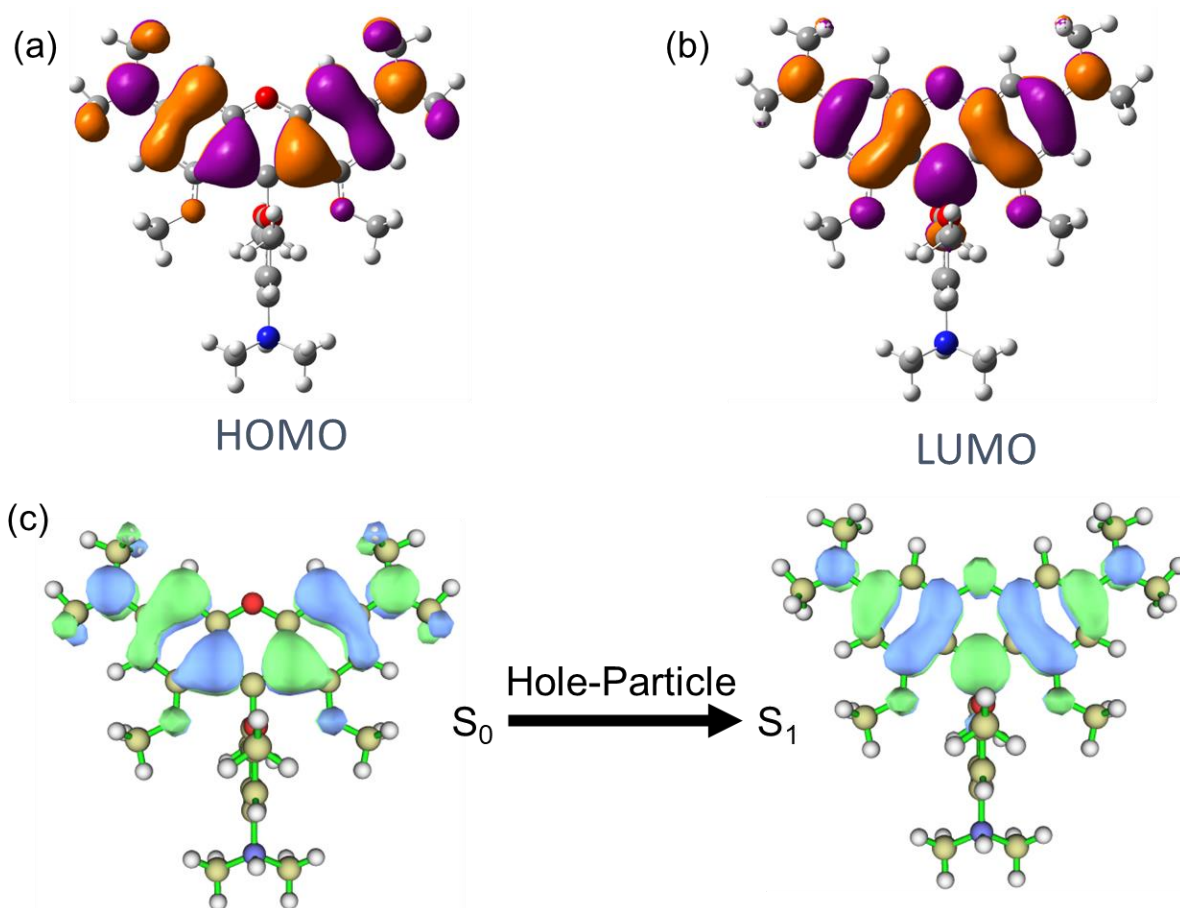


Fig. S10 (a) HOMO, (b) LUMO and the nature transition orbital analyzes of HTMARh based on the optimized S_0 state geometry.

Table S1 The theoretical calculated dipole moments of TMARh

| Compound | S_0/D | S_1/D | $\Delta_{S_0-S_1}/D$ |
|----------|---------|---------|----------------------|
| TMARh | 3.2 | 1.7 | 1.5 |

Table S2 Calculated vertical transition energy and oscillator strength of HTMARh.

| compound | Electronic transition | Energy (nm/eV) | f^a | Contrib. ^b |
|----------|-----------------------|----------------|--------|-----------------------|
| HTMARh | $S_0 \rightarrow S_1$ | 428 (2.90) | 1.0094 | H→L |

^a f means transition oscillator strength.

^b H means HOMO, L means LUMO.

Table S3. The fluorescence quantum yields of TMARh in different solvents.

| Solvent | Dielectric constant | ϕ_{fl}^a |
|------------------|---------------------|-------------------|
| MeTHF | 6.97 ¹ | 0.2 ² |
| MeCN | 37.5 ³ | 0.03 ² |
| H ₂ O | 79.7 ³ | - |

^a Data are taken from ref. 2

Table S4 Optimized geometry based on DFT calculation for TMARh in S_0 .

| | | | |
|---|-------------|-------------|-------------|
| C | 2.93438900 | -3.31819200 | 0.02668700 |
| C | 3.39010500 | -1.98950800 | 0.01575600 |
| C | 2.47863100 | -0.96992600 | 0.00917200 |
| C | 1.06965100 | -1.13440100 | 0.00973700 |
| C | 0.63343300 | -2.51216200 | 0.02914200 |
| C | 1.53396400 | -3.54377900 | 0.03481200 |
| C | 0.24817200 | 0.00953100 | -0.00560400 |
| C | 0.84302900 | 1.28608000 | -0.02350000 |
| C | 2.25787900 | 1.38627900 | -0.01037000 |
| C | 2.96404200 | 2.55755000 | -0.00932100 |
| H | 4.03979600 | 2.50428000 | 0.00389300 |
| C | 2.26947000 | 3.77830800 | -0.02749700 |
| C | 0.85183900 | 3.73952200 | -0.05285400 |
| C | 0.15869200 | 2.55853400 | -0.05442600 |
| H | 4.43735600 | -1.73728700 | 0.01435700 |
| H | 1.16863500 | -4.55426500 | 0.04764900 |
| H | 0.30540300 | 4.66442500 | -0.07574500 |
| O | 3.01249100 | 0.26858400 | 0.00418400 |
| C | -1.23042000 | -0.12911300 | 0.00159000 |
| C | -1.94137300 | -0.25840500 | -1.18197900 |
| C | -1.93941000 | -0.12456200 | 1.19330000 |
| C | -3.32092100 | -0.38504500 | -1.19193800 |
| C | -3.31890700 | -0.25222500 | 1.21956700 |
| C | -4.03211500 | -0.39700400 | 0.01884500 |
| H | -3.84207500 | -0.47454200 | -2.12842400 |
| H | -3.83790900 | -0.24165600 | 2.16142900 |
| N | 3.79576700 | -4.35025100 | 0.03091800 |
| N | 2.92366300 | 4.95274000 | -0.02374000 |
| C | 2.19636300 | 6.21331000 | -0.04493800 |
| H | 2.91023500 | 7.02968200 | -0.03126100 |

| | | | |
|---|-------------|-------------|-------------|
| H | 1.58917900 | 6.30846300 | -0.94705200 |
| H | 1.54880900 | 6.31439200 | 0.82784800 |
| C | 3.31599100 | -5.72429600 | 0.04380500 |
| H | 2.71218800 | -5.94370200 | -0.83855900 |
| H | 4.16976900 | -6.39304300 | 0.04301100 |
| H | 2.72340500 | -5.93140200 | 0.93673100 |
| C | 5.23018200 | -4.10582400 | 0.02446700 |
| H | 5.75027800 | -5.05757600 | 0.02548500 |
| H | 5.53361500 | -3.55169100 | -0.86573900 |
| H | 5.54095400 | -3.54556000 | 0.90835700 |
| C | 4.37830800 | 4.97966400 | -0.00145600 |
| H | 4.71189200 | 6.01162500 | 0.00003300 |
| H | 4.76995700 | 4.49265500 | 0.89357100 |
| H | 4.79771300 | 4.48629300 | -0.88033500 |
| O | -1.17613700 | 2.52661300 | -0.08813500 |
| O | -0.68440300 | -2.72839200 | 0.04102800 |
| O | -1.18266800 | 0.01509100 | 2.31553300 |
| O | -1.18617700 | -0.24334300 | -2.31354200 |
| C | -1.91345500 | 3.74314700 | -0.12236500 |
| H | -1.72172500 | 4.34241600 | 0.76888900 |
| H | -1.67549600 | 4.32018400 | -1.01714000 |
| H | -2.95767900 | 3.44840700 | -0.14566900 |
| C | -1.18534500 | -4.06007700 | 0.05520100 |
| H | -0.87066000 | -4.60637300 | -0.83515200 |
| H | -0.86167000 | -4.59105800 | 0.95156100 |
| H | -2.26629000 | -3.96282000 | 0.05979500 |
| C | -1.82440300 | 0.03194100 | 3.58097300 |
| H | -2.35629800 | -0.90277200 | 3.76835500 |
| H | -1.03284600 | 0.14867800 | 4.31570300 |
| H | -2.51908600 | 0.87011800 | 3.66213700 |
| C | -1.82866800 | -0.37326300 | -3.57197300 |

| | | | |
|---|-------------|-------------|-------------|
| H | -1.03782900 | -0.34003800 | -4.31594500 |
| H | -2.35875800 | -1.32436200 | -3.65024600 |
| H | -2.52496500 | 0.44878800 | -3.74834700 |
| N | -5.39923700 | -0.55708600 | 0.02907500 |
| C | -6.13352400 | -0.34238000 | 1.25946100 |
| H | -6.03204300 | 0.68206800 | 1.63684600 |
| H | -7.18720500 | -0.53643800 | 1.08017100 |
| H | -5.80320100 | -1.02761700 | 2.04150000 |
| C | -6.13556800 | -0.48748200 | -1.21670000 |
| H | -5.79983300 | -1.25372100 | -1.91683900 |
| H | -7.18758100 | -0.66887000 | -1.01553400 |
| H | -6.04244700 | 0.48876300 | -1.70720900 |

Table S5 Optimized geometry based on TDDFT calculation for TMARh in S_1 .

| | | | |
|---|-------------|-------------|-------------|
| C | -2.60481500 | 3.59408700 | -0.04090200 |
| C | -3.19058600 | 2.31576400 | -0.02329000 |
| C | -2.38945800 | 1.19169900 | -0.01337200 |
| C | -0.98481900 | 1.22919900 | -0.01369100 |
| C | -0.42014300 | 2.52838300 | -0.02472100 |
| C | -1.19642900 | 3.67590500 | -0.03523300 |
| C | -0.23969100 | 0.00000300 | -0.00006900 |
| C | -0.98491900 | -1.22913200 | 0.01358400 |
| C | -2.38955500 | -1.19151700 | 0.01336500 |
| C | -3.19077400 | -2.31551700 | 0.02333600 |
| H | -4.26186100 | -2.17163900 | 0.01701300 |
| C | -2.60510600 | -3.59388700 | 0.04089300 |
| C | -1.19672700 | -3.67582100 | 0.03511200 |
| C | -0.42034700 | -2.52836200 | 0.02454600 |
| H | -4.26168400 | 2.17197500 | -0.01688900 |
| H | -0.71341500 | 4.64018400 | -0.03773100 |
| H | -0.71379400 | -4.64014000 | 0.03756700 |

| | | | |
|---|-------------|-------------|-------------|
| O | -3.06242000 | 0.00011900 | 0.00002600 |
| C | 1.21511400 | -0.00005400 | -0.00001000 |
| C | 1.96629800 | -0.01080900 | -1.22762000 |
| C | 1.96618200 | 0.01064600 | 1.22767000 |
| C | 3.33436000 | -0.01036500 | -1.23476900 |
| C | 3.33424300 | 0.01011500 | 1.23494900 |
| C | 4.05010900 | -0.00014600 | 0.00012300 |
| H | 3.87477400 | -0.02164400 | -2.16684800 |
| H | 3.87456500 | 0.02135100 | 2.16708100 |
| N | -3.37796600 | 4.72754700 | -0.06693200 |
| N | -3.37834700 | -4.72728500 | 0.06698100 |
| C | -2.75563600 | -6.03192700 | -0.03906600 |
| H | -3.52689900 | -6.79961200 | 0.01044300 |
| H | -2.20789700 | -6.15656000 | -0.98281700 |
| H | -2.05677200 | -6.20802600 | 0.78615100 |
| C | -2.75514000 | 6.03214100 | 0.03902200 |
| H | -2.05632200 | 6.20814800 | -0.78625400 |
| H | -3.52634100 | 6.79988800 | -0.01046300 |
| H | -2.20732200 | 6.15676500 | 0.98272800 |
| C | -4.81844200 | 4.61643300 | 0.05348700 |
| H | -5.25857800 | 5.61155100 | 0.00118500 |
| H | -5.24048400 | 4.02053000 | -0.76313000 |
| H | -5.12147200 | 4.15590800 | 1.00323800 |
| C | -4.81882500 | -4.61605400 | -0.05328500 |
| H | -5.25903900 | -5.61113400 | -0.00091400 |
| H | -5.24072800 | -4.02010000 | 0.76336700 |
| H | -5.12192300 | -4.15552100 | -1.00301100 |
| O | 0.93721400 | -2.56381200 | 0.02050700 |
| O | 0.93742200 | 2.56372200 | -0.02079700 |
| O | 1.19944900 | 0.02149400 | 2.31905200 |
| O | 1.19966700 | -0.02161200 | -2.31907100 |

| | | | |
|---|------------|-------------|-------------|
| C | 1.60571600 | -3.81367500 | 0.03568500 |
| H | 1.35627600 | -4.38474600 | 0.93573000 |
| H | 1.36055800 | -4.40417700 | -0.85293300 |
| H | 2.67010200 | -3.58026500 | 0.03562300 |
| C | 1.60602500 | 3.81352900 | -0.03614000 |
| H | 1.35649600 | 4.38457300 | -0.93617700 |
| H | 1.36105100 | 4.40409800 | 0.85248400 |
| H | 2.67039200 | 3.58003000 | -0.03622900 |
| C | 1.82774200 | 0.03209500 | 3.59758900 |
| H | 2.44187600 | 0.92900300 | 3.71884800 |
| H | 1.01792800 | 0.03761200 | 4.32456700 |
| H | 2.44269900 | -0.86218000 | 3.73317200 |
| C | 1.82807700 | -0.03222700 | -3.59755000 |
| H | 1.01833000 | -0.03766700 | -4.32460400 |
| H | 2.44311100 | 0.86200800 | -3.73305300 |
| H | 2.44215800 | -0.92917500 | -3.71877500 |
| N | 5.38845000 | -0.00018500 | 0.00017200 |
| C | 6.13788000 | -0.00730400 | 1.25567300 |
| H | 5.88625400 | -0.88683500 | 1.85338500 |
| H | 7.20103800 | -0.03782000 | 1.03141800 |
| H | 5.93204800 | 0.89461500 | 1.83802700 |
| C | 6.13794800 | 0.00687600 | -1.25528700 |
| H | 5.88637100 | 0.88639400 | -1.85303900 |
| H | 7.20109600 | 0.03737400 | -1.03097900 |
| H | 5.93212000 | -0.89505600 | -1.83762400 |

Table S6 Optimized geometry based on DFT calculation for HTMARh in S_0 .

| | | | |
|---|------------|-------------|-------------|
| C | 2.63191300 | -3.55380500 | -0.05068700 |
| C | 3.20889000 | -2.27155100 | -0.05792900 |
| C | 2.39768000 | -1.17253900 | -0.03081900 |
| C | 0.97927000 | -1.21076700 | 0.00791100 |
| C | 0.41765400 | -2.54090100 | 0.00872800 |

| | | | |
|---|-------------|-------------|-------------|
| C | 1.21583900 | -3.65093200 | -0.01766000 |
| C | 0.26956200 | 0.00121700 | 0.04064400 |
| C | 0.96881700 | 1.21954800 | 0.03241900 |
| C | 2.38711400 | 1.19442500 | -0.01845900 |
| C | 3.18796700 | 2.30095700 | -0.04699400 |
| H | 4.25471300 | 2.15771200 | -0.08766500 |
| C | 2.59953300 | 3.57782100 | -0.02437300 |
| C | 1.18343100 | 3.66182800 | 0.03420400 |
| C | 0.39579100 | 2.54435800 | 0.06316900 |
| H | 4.27466500 | -2.11832100 | -0.08608700 |
| H | 0.75860600 | -4.62345500 | -0.01526900 |
| H | 0.71778800 | 4.63006100 | 0.05764400 |
| O | 3.03891500 | 0.01393900 | -0.04397100 |
| C | -1.22005800 | -0.00636500 | 0.07893900 |
| C | -1.94446300 | 0.03044900 | -1.10578400 |
| C | -1.88619700 | -0.05288900 | 1.29408800 |
| C | -3.33463000 | 0.02024800 | -1.08835600 |
| C | -3.27805200 | -0.06656600 | 1.33514600 |
| C | -3.95969300 | -0.03001900 | 0.13934900 |
| H | -3.89818300 | 0.05053600 | -2.00672000 |
| H | -3.80930100 | -0.10406300 | 2.27442200 |
| N | 3.39343400 | -4.65909200 | -0.07551400 |
| N | 3.35051000 | 4.69012600 | -0.05605500 |
| C | 2.73484200 | 6.00950800 | -0.03513700 |
| H | 3.51648100 | 6.76051800 | -0.06726600 |
| H | 2.08440300 | 6.15856300 | -0.89875400 |
| H | 2.15355900 | 6.16308700 | 0.87562400 |
| C | 2.78975600 | -5.98414900 | -0.06964700 |
| H | 2.15647500 | -6.13685500 | -0.94529200 |
| H | 3.57886000 | -6.72771900 | -0.08964100 |
| H | 2.19355100 | -6.14567500 | 0.83002100 |

| | | | |
|---|-------------|-------------|-------------|
| C | 4.84455300 | -4.54844500 | -0.11146800 |
| H | 5.27314900 | -5.54449900 | -0.12655400 |
| H | 5.17898300 | -4.01832000 | -1.00500300 |
| H | 5.22324100 | -4.02627200 | 0.76894000 |
| C | 4.80174400 | 4.59293500 | -0.11778500 |
| H | 5.22089900 | 5.59287900 | -0.13850100 |
| H | 5.20090500 | 4.07269400 | 0.75469000 |
| H | 5.12503100 | 4.06753900 | -1.01818300 |
| O | -0.93748200 | 2.61521500 | 0.12202800 |
| O | -0.91591800 | -2.62438100 | 0.03628200 |
| O | -1.10460900 | -0.08468100 | 2.39225500 |
| O | -1.21110600 | 0.07480900 | -2.23657400 |
| C | -1.58023000 | 3.88558100 | 0.14978300 |
| H | -1.28568600 | 4.45226800 | 1.03389000 |
| H | -1.35512700 | 4.45602400 | -0.75212400 |
| H | -2.64349700 | 3.67193700 | 0.19060900 |
| C | -1.54753600 | -3.90057300 | 0.04458800 |
| H | -1.30314600 | -4.46233800 | -0.85775200 |
| H | -1.26172900 | -4.47108200 | 0.92910600 |
| H | -2.61324900 | -3.69670000 | 0.07037300 |
| C | -1.71711500 | -0.13115100 | 3.67663100 |
| H | -2.31625300 | -1.03558100 | 3.79251400 |
| H | -0.90153800 | -0.14439900 | 4.39266300 |
| H | -2.33582400 | 0.75106200 | 3.84765200 |
| C | -1.87832200 | 0.11400800 | -3.49341000 |
| H | -1.09429800 | 0.14264900 | -4.24345000 |
| H | -2.48889900 | -0.77810300 | -3.64072800 |
| H | -2.49686200 | 1.00853500 | -3.58095400 |
| N | -5.43665300 | -0.04297900 | 0.19477400 |
| C | -6.03205500 | -1.24306600 | -0.47656500 |
| H | -5.57527100 | -2.13337800 | -0.05670300 |

| | | | |
|---|-------------|-------------|-------------|
| H | -7.10196700 | -1.23803300 | -0.29246100 |
| H | -5.83651300 | -1.18382800 | -1.54180200 |
| C | -6.04537500 | 1.23073800 | -0.30798100 |
| H | -5.84404800 | 1.32043800 | -1.36998600 |
| H | -7.11578400 | 1.18758100 | -0.13085600 |
| H | -5.60207500 | 2.06029400 | 0.23343800 |
| H | -5.68527900 | -0.11077300 | 1.18230000 |

Reference

1. D. F. Aycock, *Organic Process Research & Development*, 2007, **11**, 156-159.
2. T. J. Sorensen, D. Shi and B. W. Laursen, *Chem-Eur J*, 2016, **22**, 7046-7049.
3. I. M. Smallwood, *Handbook of Organic Solvent Properties*, Arnold, Great Britain, 1996.